FINAL REPORT

on

ASSESSMENT OF GEOTEXTILE FABRIC COMPATIBILITY WITH LEACHATE EXTRACTED FROM VICKERY (OHIO) SLUDGE

to

CHEMICAL WASTE MANAGEMENT, INC.

9/24/85

September 24, 1985

by

B. W. Vigon, A. J. Pollack, R. E. Sharpe, J. W. Brasch,
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EXECUTIVE SUMMARY

Chemical Waste Management, Inc., has contracted with Battelle's Columbus Division to evaluate four geotextile samples for their compatibility with leachate generated from their Vickery, Ohio, facility. Although no EPA methods directly address compatibility studies for geotextile materials, every attempt was made to maintain the overall spirit of EPA Method 9090.

Geotextiles perform two functions in the closure cell and specific analytical tests were designed to evaluate the capability of the material to perform its intended functions over an extended time period. One function of a geotextile is to filter fine particles that may eventually clog the leachate collection system. A second function is to stabilize the cell layers to maintain the mechanical integrity of the cell. Fiber cracking, swelling, strength loss and decomposition are undesirable changes from the standpoint of geotextile performance. The leachate tested was generated using a modified EP extraction procedure (EP) applied to unfixed sludge. This leachate should provide a more severe exposure test for the geotextile fabrics than will actually be encountered in the closure cells with fixed sludge.

The polyester and polypropylene geotextile samples were exposed to the leachate for a period of 60 days. The material was submerged in the leachate at an elevated temperature of 65 C to simulate exposure to leachate at ambient temperature for a period of 25 years. Samples of the materials were removed from the exposure chambers at 15, 30, 45, and 60 days. These specimens were analyzed by both macroscopic and microscopic methods to determine whether the integrity of any of the four materials was being degraded by exposure to the leachate.

The Mullen Burst Test, widely used in industry for testing of fibrous materials, was employed to provide macroscopic property information on each of the four types of geotextile samples. Comparisons were made between the starting material, samples exposed to distilled water at 65 C, and samples exposed to leachate at 65 C. There was no significant difference in strength between burst test values for controls and exposed specimens.

Visual examination of the samples was performed using polarized light microscopy and scanning electron microscopy. These two methods provided comparable observations which indicated a lack of physical degradation of any of the polymeric fibers. The only noticeable change in the samples was the adherence of leachate-related particulate materials to the fibers. Both polyester fabrics showed some indication of stress prior to exposure. No swelling, cracking, or stressing of the samples was attributable to the exposure test.

Fourier-Transform Infrared Spectroscopy was employed to determine if the chemical structure of the polyester and polypropylene fibers changed as a result of exposure to the leachate. Artifacts noted in the spectra during this test indicate the adhesion of fine leachate particles. The overall evaluation indicates that no significant chemical changes in the polymers occurred due to exposure to Vickery leachate.

In conclusion, the test results showed no evidence of significant deterioration in any of the geotextile specimens at the end of any period up to and including 61 days of exposure to the Vickery leachate. The appearance, chemical makeup, or integral strength of the geotextile fabrics were not compromised in any way by the exposure process.

Based on these extensive tests, it is concluded that these geotextile materials will be compatible for a minimum of 25 years with leachate of the type that could be potentially generated from the Vickery, Ohio, facility.

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INTRODUCTION

Chemical Waste Management, Inc., is in the process of engineering closure cells to contain the sludge materials now found at their facility in Vickery, Ohio. Before deposition, the sludge will go through a chemical fixation process that will improve the handling and physical characteristics of the waste, decrease the surface area across which transfer or loss of contained pollutants can occur, and limit the solubility of constituents contained in the waste.

The U.S. Environmental Protection Agency (EPA) has required that laboratory testing be done to confirm the long-term compatibility of liners with the leachate in the closure cell. In this case, however, the specific materials being evaluated are four geotextile samples (two polypropylene and two polyester) that will act as a permeable filtration matrix incorporated in the closure cell. This material will be a particulate barrier that will allow any leachate from the site to pass through it and eventually be collected and treated.

To determine the compatibility of the geotextile samples with the leachate, we employed an exposure environment consistent with EPA Method 9090. Although this method does not specifically address geotextile materials, it does apply to polymeric liners, and geotextiles are polymeric in nature. Therefore, the spirit of the 9090 test was incorporated in this testing. The method involves testing at an elevated temperature of 50 C to produce exposure conditions that accelerate the actual exposure time to that expected in 25 years of field exposure at ambient temperature. To reduce the length of the exposure period to 60 days, the geotextile samples were exposed to the leachate at a temperature of 65 C. This time and temperature combination corresponds to an acceleration factor in excess of the EPA 9090 required value of 152. Samples were also exposed to leachate at 10 C, and a set of controls was exposed to distilled water at 65 C.

Presently, there is no leachate available from the Vickery facility so a liquid leachate was generated from unfixed sludge. This was done using a modification of the EPA Extraction Procedure (EP). Since the sludge will go through the fixation process before incorporation into the closure cell, the use of unfixed sludge for the laboratory test should provide a more extreme exposure condition for the geotextiles.

The following sections describe the methodology for generating the leachate, results of the physical examinations and chemical testing, and the conclusions based on those tests for geotextile stability.

METHODOLOGY AND MATERIALS

This study was conducted using EPA-approved protocols (Method 9090) to the extent possible. In particular, the leachate exposure conditions are comparable to those called for by Method 9090. Since geotextiles and not liner materials are being evaluated, it was desirable to perform the types of tests tailored to measure changes in properties of importance to the maintenance of fabric performance. However, wherever possible, the overall spirit of 9090 was maintained.

Geotextile Samples

Four different geotextile materials were exposed to the leachate. The two polyester samples were Trevira 11200, which is a spunbond continuous fiber mat, and Trevira 21250, which is a noncontinuous filament mat. The two polypropylene materials were Fibretex 400 and Typar 3601, a heat set material.

Enough geotextile material was exposed to leachate at 10 C and 65 C so that samples would be available for physical/chemical testing at 15, 30, 45, and 60 days. Also, control samples were subjected to 65 C temperatures immersed in distilled water.

EP Leachate Generation

Approximately 25 gallons of liquid leachate were generated for the geotextile exposure tests. The leachate was prepared in 5-gallon lots and was obtained by combining 933.5 grams of raw Vickery, Ohio, sludge with 15 liters of Barnstead deionized water. Because of the volume of material being handled, a motor-driven paddle stirrer was employed instead of a tumbling extractor. During the leachate generation process, agitation was maintained for a period of 24 hours, and efforts were made to contain all volatiles by sealing the extraction vessel and by minimizing head space. The pH of the solution was monitored using a meter that was calibrated to pH 4.0 and 7.0. All five lots had pH measurements at or slightly below 2.0 (actual pH range was from 1.67 to 2.10). Therefore, in accordance with the EP protocol (Method 1310), no acetic acid was added to the leachate during or after the extraction

process. After the 24-hour period, deionized water was added, with agitation, to bring the final volume up to 19.785 ℓ (5 gallons). The leachate was then passed through a 75-μm sieve, placed into a container, sealed, and stored at 4 C until used in the exposure test. Any material retained on the sieve was returned to the original sludge container.

The liquid supernatant portion of the EP leachate was used for the exposure test described below.

Test Apparatus and Preparation of Samples

The geotextile samples were cut into 4" x 4" patches and placed into sample racks that were constructed of stainless steel. The stainless steel was coated with Xylan to prevent any rack degradation during the exposure period. The racks were designed to hold the samples in a vertical position while preventing contact with other samples or the bottom or sides of the containment vessels. The design allowed thorough circulation of the leachate.

Exposure tests were conducted at two temperatures, 10 C and 65 C. The low temperature vessels were older, chromatography jar-type chambers fitted with a paddle stirrer. The combination of low temperature and sealed tops made it possible to easily contain any volatiles associated with the leachate during the exposure period. The 65 C chambers were cylindrical kettle-type chambers fitted with a sealed lid. Agitation was accomplished through the use of Teflon-coated magnetic stir bars.

Control samples were also exposed to 65 C temperature distilled water to isolate the effects of elevated temperature on the geotextile samples.

After the prescribed exposure period, samples were removed from the leachate and cleaned prior to examination. The cleaning process consisted of a water rinse, an ethanol wash, a second water rinse, and drying (see Appendix B for complete procedure). It was verified by both microscopic and spectrophotometric analytical methods that this method of sample preparation did not result in any alteration of the geotextile samples.

Both the cleaning process specimens and subsequent exposure samples were compared with virgin materials and controls to determine if any degradation such as swelling or cracking of the fibers or if any chemical transformations were taking place.

ANALYTICAL METHODS

Mullen Burst Test

The Mullen Burst Test is a procedure widely used by the paper industry to determine the bursting strength of a fibrous material. The test consists of inflating a rubber bladder against a sample held in a die until the sample fails. The pressure necessary to bring about the failure is recorded on a pressure gauge in pounds per square inch. The tests were performed using a Mullen Tester, Model 64-A-210, in a controlled temperature room at 72 F, with 5 percent relative humidity.

Microscopy

The bulk of the visual examinations of the samples was performed with polarized light microscopy (PLM). A Leitz Orthoplan Microscope was used for this work and micrographs were taken with Polaroid Type-55 film.

Fibers from each of the geotextile materials were removed from the bulk material and placed on a glass slide in immersion oil for examination. Extreme care was taken when separating the samples so as not to pull or otherwise stress the individual fibers in any way. This procedure was followed for both controls and exposed specimens.

For a more detailed evaluation of the surface conditions of the fibers, Scanning Electron Microscopy (SEM) was used. A small portion of each geotextile was removed and gold coated for examination on an I.S.I., Super 3, Scanning Electron Microscope.

Fourier-Transform Infrared Spectroscopy

The FT-IR technique is a means of obtaining spectral information to qualitatively assess the changes in internal (structural) chemical bonding of the geotextile material when exposed to leachate. Although the acquisition of spectra using FT-IR is straightforward and quite simple, the interpretation of this spectral information requires experience.

The analysis of the samples was performed with a Digilab FTS-10 (x38666) Spectrometer using a wide range MCT detector. The samples were run in the attenuated total reflectance (ATR) mode using a 45° Germanium crystal.

RESULTS

Testing Temperature

The average temperature and the variation over time under which exposure of specimens was conducted are presented in Table 1.

TABLE 1. TEMPERATURE VARIATIONS OBSERVED IN EXPOSURE TANKS, C

Temperature	Trevira 11200	Trevira 21250	Typar 3601	Fibretex 400
10 C Exposure to Leachate				
Minimum	12.8	12.8	12.8	12.8
Average	14.9	15.4	15.4	15.4
Maximum	19.4	19.4	19.4	19.4
65 C Exposure to Leachate				
Minimum	61.0	63.0	63.0	64.0
Average	64.5	64.3	64.8	65.4
Maximum	66.0	65.0	68.0	67.0
65 C Exposure to Distilled Water (Controls)				
Minimum	64.4	64.4	64.4	63.8
Average	65.4	65.1	65.2	64.9
Maximum	66.1	67.8	66.7	66.1

Because of the elevated temperatures in the laboratory environment, it was difficult to obtain the 10 C exposure temperature. These test samples, therefore, were subjected to slightly more severe conditions than would be expected at a 10 C temperature. This slightly elevated baseline temperature does not appear to have had any impact upon the overall results and conclusions.

Mullen Burst Test Results

The burst test results were expected to provide macroscopic property information on the geotextiles in a manner analogous to the strength testing incorporated in Method 9090. In addition, this test was anticipated to correlate any changes noted in the microscopic and spectroscopic examinations.

A total of 119 samples were analyzed. There were 10 replicates of each geotextile run on the unexposed starting material; 10 replicates of each geotextile that had been exposed for 60 days to 65 C leachate and subsequently cleaned, and 10 replicates of the 60-day, 65 C controls immersed in distilled water that had also gone through the cleaning procedure. There were only 9 replicate samples available for the Trevira 11200, 60-day, 65 C distilled water sample accounting for the total of 119 samples instead of 120.

The mean burst test values and standard deviations for the various geotextile samples are shown in Table 2.

In general, the closeness of the test means to the control means suggested no degradation due to leachate exposure (Figure 1). However, in order to more critically evaluate the results of the burst test, a statistical analysis of the values was performed using the Student's t-test.

The equations used in the t-test analysis are the following.

$$t = \frac{\bar{x}_1 - \bar{x}_0}{s\left(\frac{1}{n_1} + \frac{1}{n_0}\right)^{\frac{1}{2}}}$$

$$s^2 = (f_1 s_1^{\,2} + f_0 s_0^{\,2})/(f_1 + f_0)$$

where

$\bar{x}_1$ = average property value for test specimens
$\bar{x}_0$ = average property value for control specimens
n_1 = number of test specimen measurements
n_0 = number of control specimen measurements
s_1 = standard deviation for number of test measurements in $\bar{x}_1$
s_0 = standard deviation for number of control measurements in $\bar{x}_0$
f_1 = degrees of freedom for s_1^2 ($f_1 = n_1-1$)
f_0 = degrees of freedom for s_0^2 ($f_0 = n_0-1$)
s^2 = weighted average variance for test and control measurements.

TABLE 2. GEOTEXTILE BURST TEST RESULTS[a]

	mean	std. dev.
Trevira 11200		
Starting Material	302	21.7
Treatment (Leachate Exposure)	295	18.6
Control (Water Exposure)	302	28.8
Trevira 21250		
Starting Material	238	28.0
Treatment (Leachate Exposure)	205	22.1
Control (Water Exposure)	204	15.1
Typar 3601		
Starting Material	291	20.6
Treatment (Leachate Exposure)	293	19.9
Control (Water Exposure)	290	16.2
Fibretex 400		
Starting Material	325	22.8
Treatment (Leachate Exposure)	335	31.1
Control (Water Exposure)	344	34.9

(a) Mean and Standard Deviation in pounds per square inch (gage).

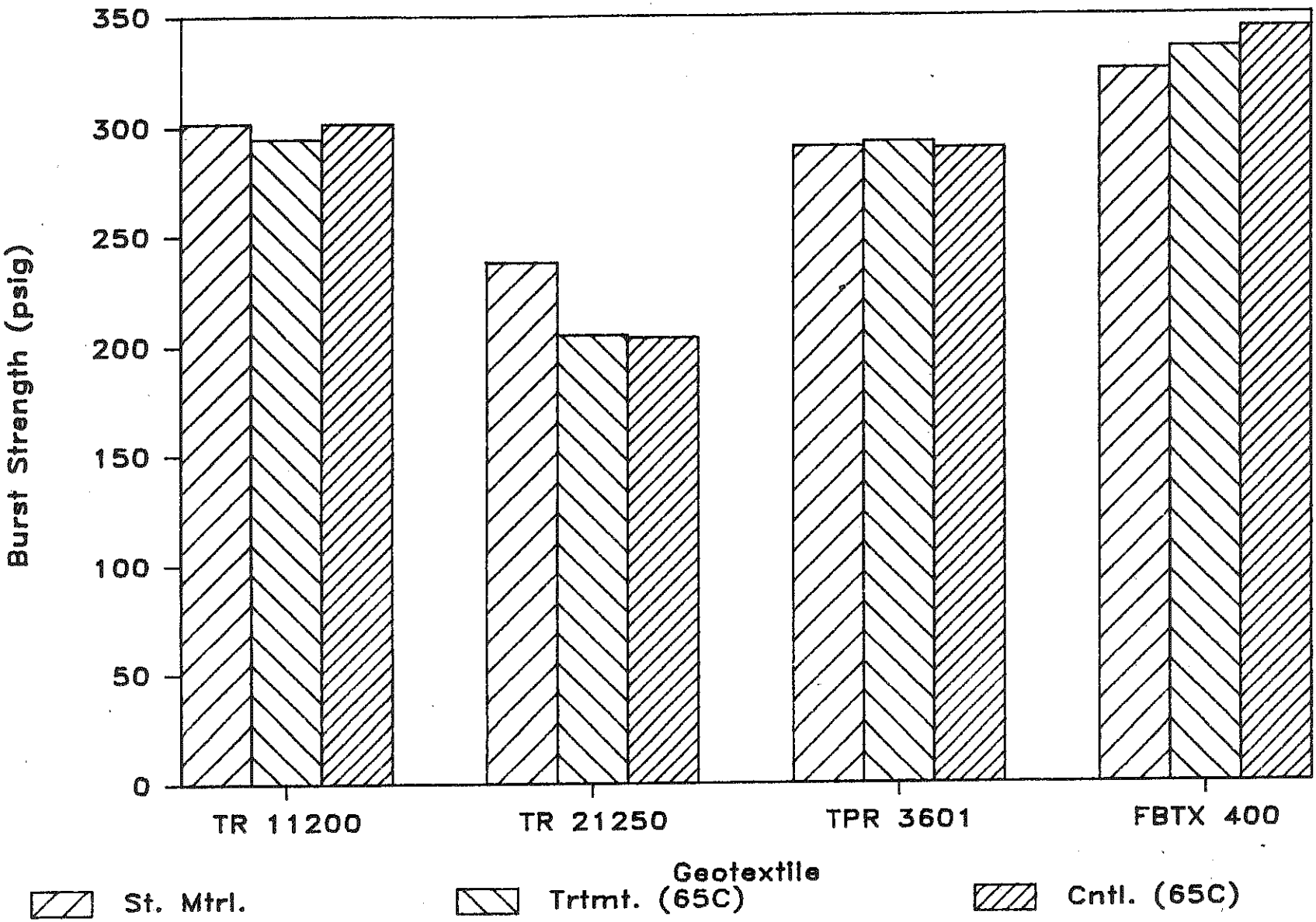

FIGURE 1. GEOTEXTILE BURST STRENGTH

Two sets of statistical calculations were made using the Student's t-test. First, the mean values of the four control (water exposed) materials were compared with the mean values of the four starting materials; thus, the stress on the geotextile due to the increased temperature could be analyzed before determining the effects of leachate. Second, comparisons of the mean values of the treated (leachate exposed) materials with the mean values of the control (water exposed) materials were made to determine whether exposure to the leachate produced any degradation in the geotextiles.

The results of the t-tests indicated no detrimental effects on Trevira 11200, Typar 3601, and Fibretex 400. However, the t-test comparing the mean value of the control for Trevira 21250 with the starting material had a value greater than the critical "t" value of 2.26. Therefore, an increase in temperature did produce a significant change, at the 5 percent level, in the strength of this material. Leachate exposure to Trevira 21250, however, caused no significant change. Table 3 summarizes the t-test data.

The overall indications of the Mullen Burst Test are that none of the four geotextile materials suffered a loss of physical strength due to exposure to the leachate at 65 C for 60 days.

TABLE 3. T-TEST RESULTS FOR BURST TEST

	Comparison of Control (Water Exposed) Material Starting Material with Control	Comparison of Treated (Leachate Exposed) Material with Control (Water Exposed) Material
Trevira 11200	0.00	0.64
Trevira 21250	3.38(a)	0.12
Typar 3601	1.44	0.61
Fibretex 400	0.12	0.37

(a) Number exceeds the critical value of 2.26. Therefore, there is a significant loss in textile strength due to heating.

Microscopy Results

An initial evaluation of each of the four samples was performed to set baseline-inherent properties of the polymeric fibers. This examination resulted in the determination of the following features.

Trevira 11200 - Long, continuous round fibers that were consistent in diameter; surface of fibers appears smooth; lots of ends evident because continuous fibers were severed during sample preparation; stress features evident, especially at bends in the fibers (Figure 2).

Trevira 21250 - Mostly smooth, round fibers; fibers have varying diameters; evidence of some flattened, ribbon-like fibers; stress features evident (identified as lines across the fibers, especially at bends); number of stressed fibers greater in the Trevira 21250 than in the Trevira 11200 (Figure 3).

Typar 3601 - Continuous fiber matrix; fiber diameters are consistent; smooth surfaces; stress lines not evident; any change in fiber diameter is probably due to heat set during the manufacturing process (Figure 4).

Fibretex 400 - Smooth fibers; they vary from round to ribbon-like along the length of a single fiber; ribbon effect is probably due to some manufacturing process, i.e., pressure or heat; stress lines not evident (Figure 5).

With this baseline information in place, samples from the 15, 30, 45, and 60-day exposure periods were examined. Both the high and low temperature specimens were looked at, and polarized light microscopy did not indicate that any degradation of any of the four geotextile materials was taking place. There was no increase in stress lines, and new cracks and crazes were not observed. Micrographs were taken comparing the 61-day water controls and the 61-day high-temperature leachate specimens and are presented in Figures 6 through 13.

Scanning Electron Microscopy (SEM) afforded a more detailed look at the fibers at a higher resolution with a greater depth of field. Since no pronounced degradation was observed with polarized light microscopy (PLM), the SEM was used on a limited basis.

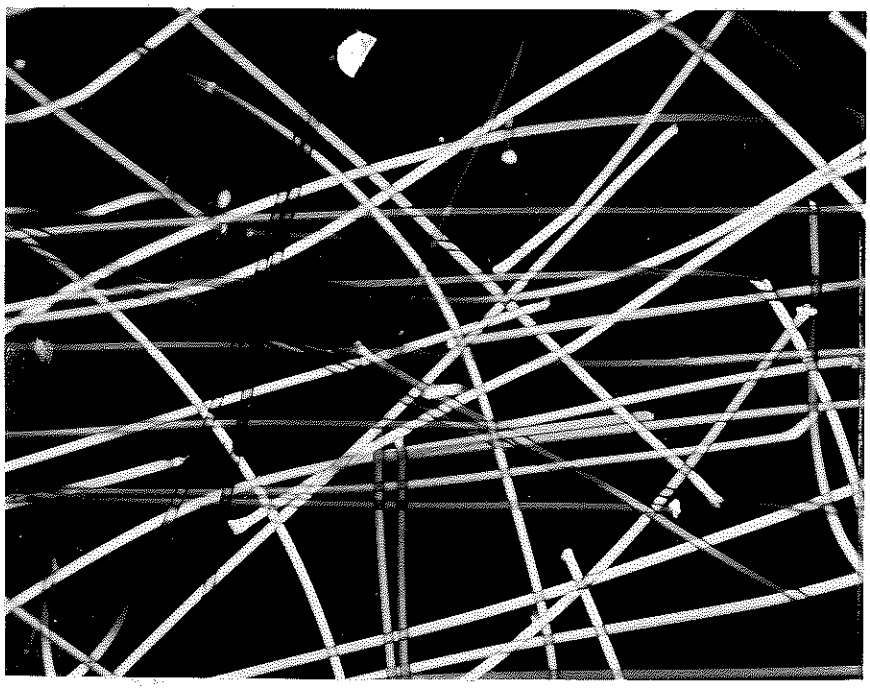

FIGURE 2. TREVIRA 11200
STARTING MATERIAL, POLARIZED LIGHT MICROGRAPH, 50x

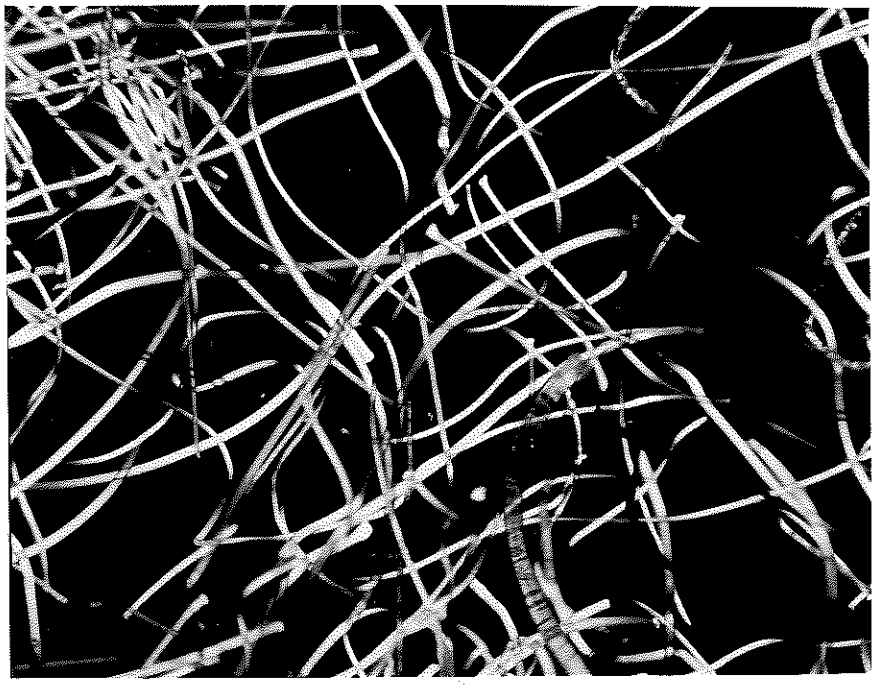

FIGURE 3. TREVIRA 21250
STARTING MATERIAL, POLARIZED LIGHT MICROGRAPH, 50x

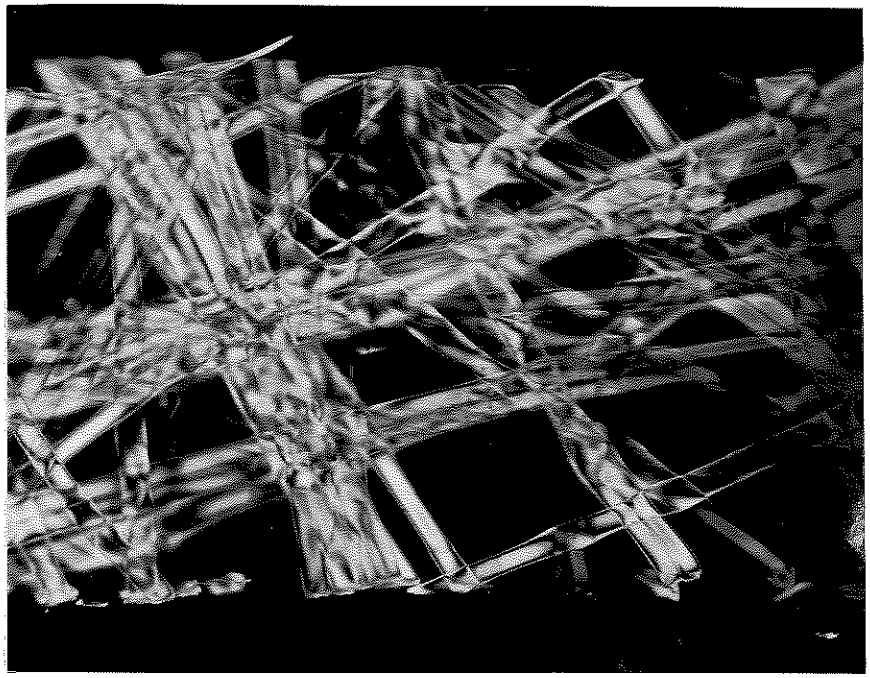

FIGURE 4. TYPAR 3601
STARTING MATERIAL, POLARIZED LIGHT MICROGRAPH, 64x

FIGURE 5. FIBRETEX 400
STARTING MATERIAL, POLARIZED LIGHT MICROGRAPH, 50x

FIGURE 6. TREVIRA 11200
61 DAY, 65 C WATER CONTROL, POLARIZED LIGHT MICROGRAPH, 250x

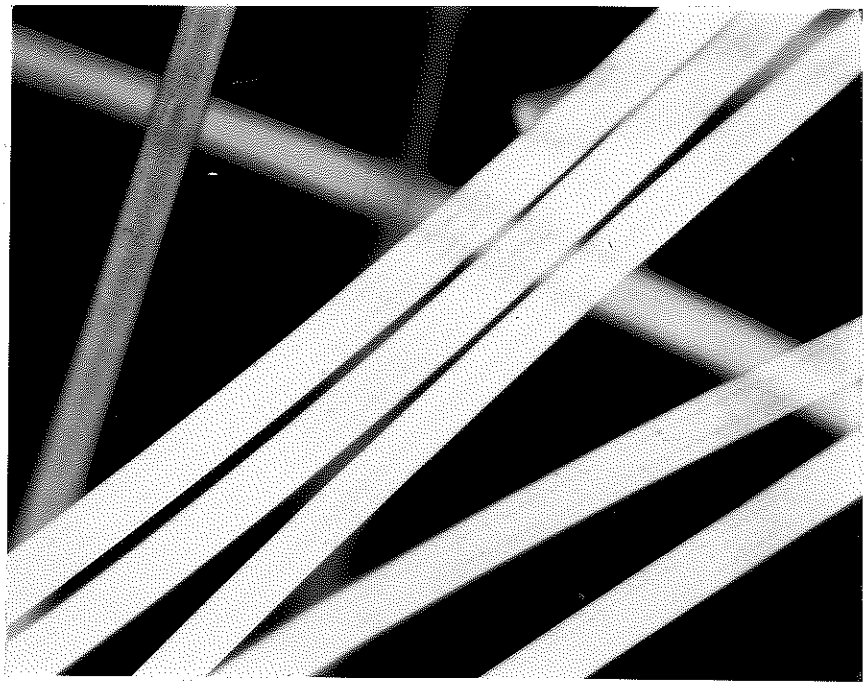

FIGURE 7. TREVIRA 11200
61 DAY, 65 C LEACHATE EXPOSED, POLARIZED LIGHT MICROGRAPH, 250x

FIGURE 8. TRIVERA 21250
61 DAY, 65 C WATER CONTROL, POLARIZED LIGHT MICROGRAPH, 250x

FIGURE 9. TREVIRA 21250
61 DAY, 65 C LEACHATE EXPOSED, POLARIZED LIGHT MICROGRAPH, 250x

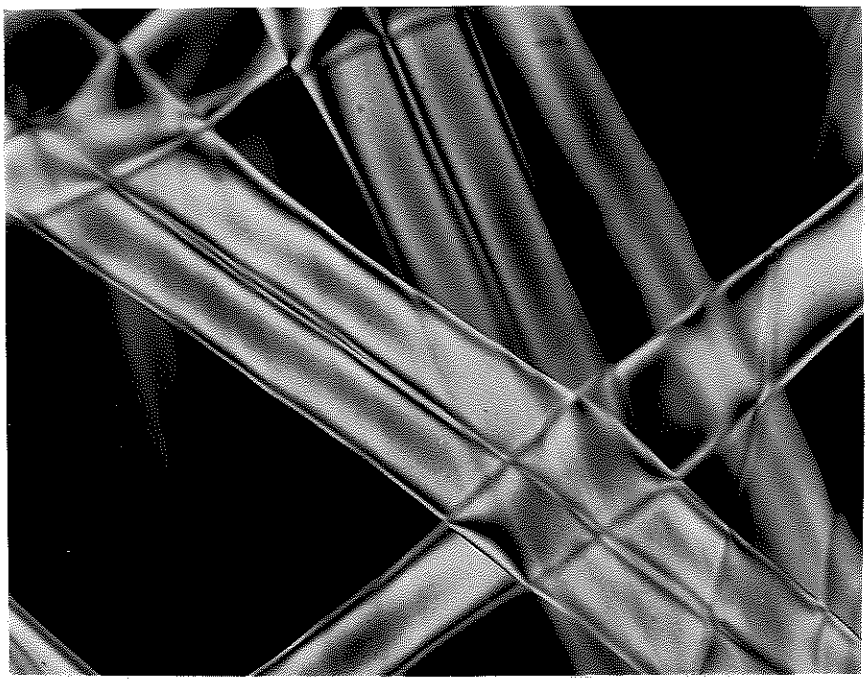

FIGURE 10. TYPAR 3601
61 DAY, 65 C WATER CONTROL, POLARIZED LIGHT MICROGRAPH, 250x

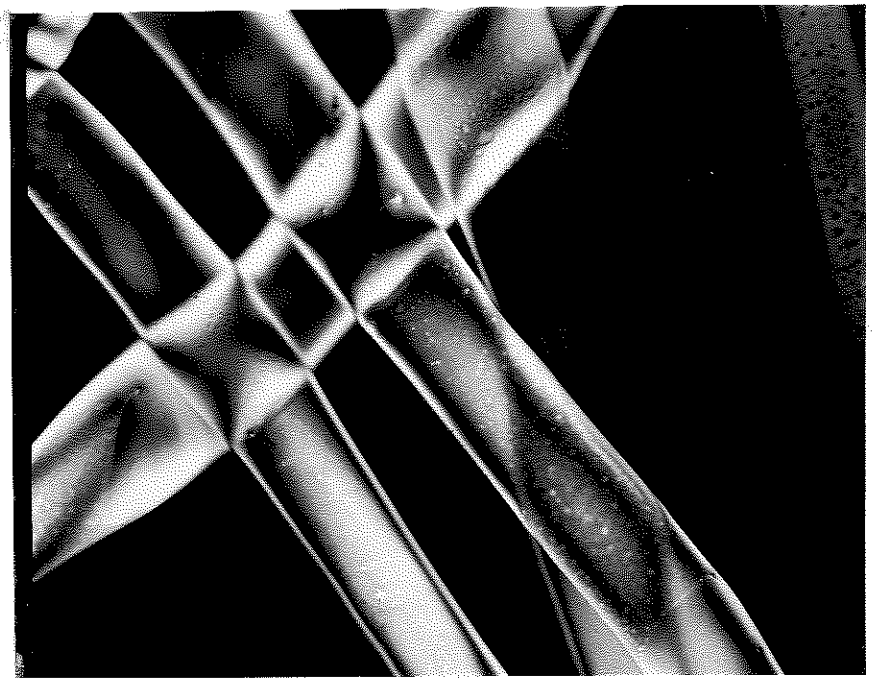

FIGURE 11. TYPAR 3601
61 DAY, 65 C LEACHATE EXPOSED, POLARIZED LIGHT MICROGRAPH, 250x

FIGURE 12. FIBRETEX 400
61 DAY, 65 C WATER CONTROL, POLARIZED LIGHT MICROGRAPH, 250x

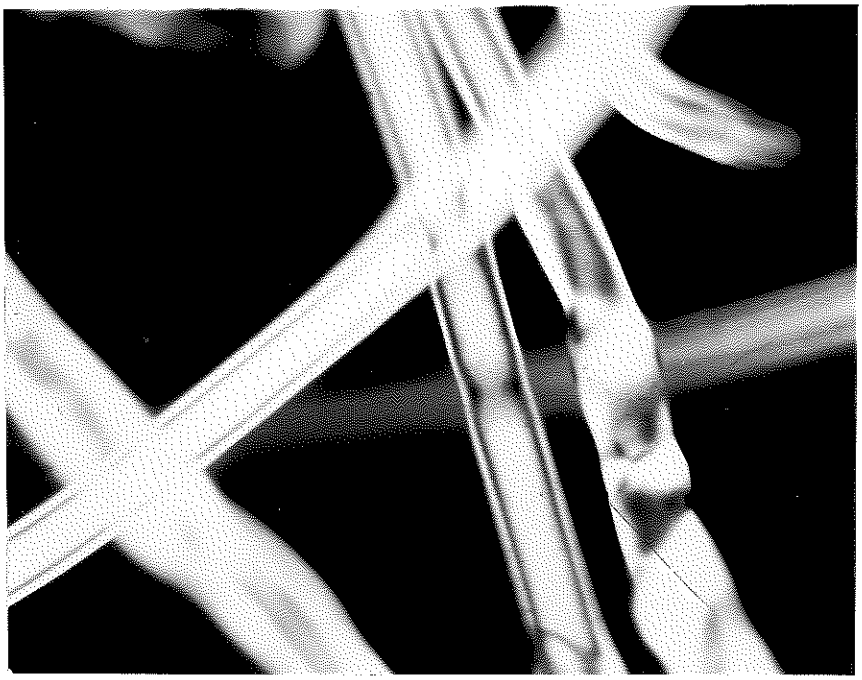

FIGURE 13. FIBRETEX 400
61 DAY, 65 C LEACHATE EXPOSED, POLARIZED LIGHT MICROGRAPH, 250x

A comparison of the high-temperature water controls versus the high temperature leachate specimens confirmed the PLM observations. The surface of the four exposed geotextiles did not exhibit any gross etching or pitting when compared to the controls (Figures 14 through 21).

The only major difference between the controls and the leachate-exposed specimens was the presence of a considerable amount of very fine debris on the surface of the fibers. However, it was felt that in order to clean the samples to a point where the surface would be clean by SEM, the process would have to be so vigorous that the integrity of the fibers may be compromised by the cleaning process itself. Although the adhering particles appear dramatic, they represent a very small quantity of material.

The results of the polarized light and scanning electron microscopy are in agreement. As shown in the micrographs, there has been no gross change in the shape or surface features in the fibers after exposure to the leachate. The ends of the fibers have not become frayed and the general appearance of the material is consistent with the controls. There are no stress lines, as observed at the bends in the controls, located anywhere along the straight portions of the fibers in the polarized light micrographs. This would have indicated stress due to leachate exposure. There is no evidence of the fibers cracking either by PLM or SEM. Overall, there is a visual consistency between the fiber characteristics when controls and leachate exposed specimens are compared.

This shows that the exposure of these geotextile materials to leachate that could be potentially generated from the Vickery facility does not result in observable physical degradation of the polymeric fibers.

Fourier-Transform Infrared Spectroscopy (FT-IR) Results

The initial use of the FT-IR was to confirm that the cleaning procedure did not degrade the geotextile samples. The analysis of the spectra of cleaned versus noncleaned specimens showed that no degradation was taking place.

Samples of the 65 C geotextiles were evaluated at the 15-day time period and compared to starting material spectra. The Trevira 21250 and Trevira 11200 displayed no significant change in spectra, which indicates that

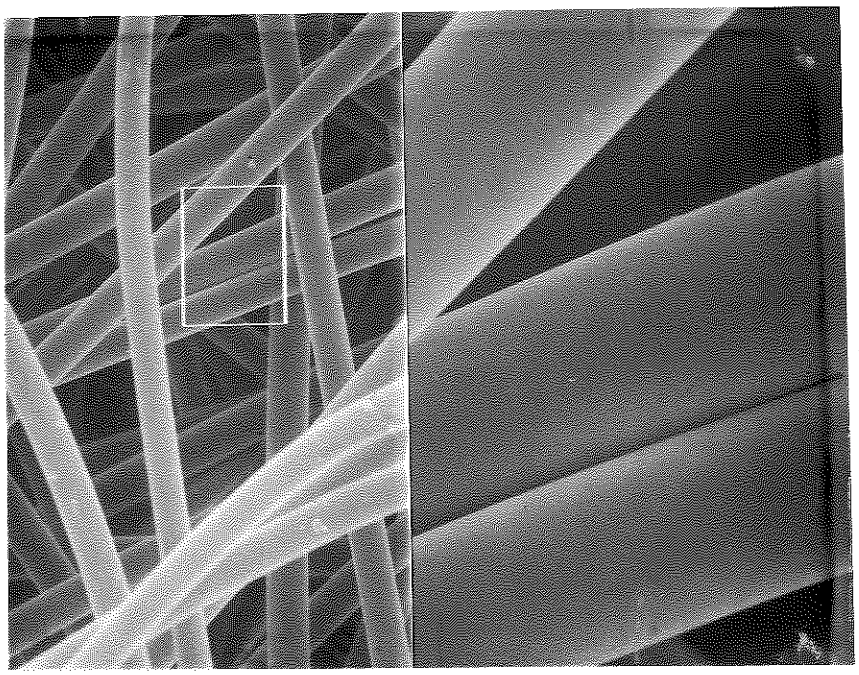

FIGURE 14. TREVIRA 11200
61 DAY, 65 C WATER CONTROL, SCANNING ELECTRON MICROGRAPH, 200/1000x

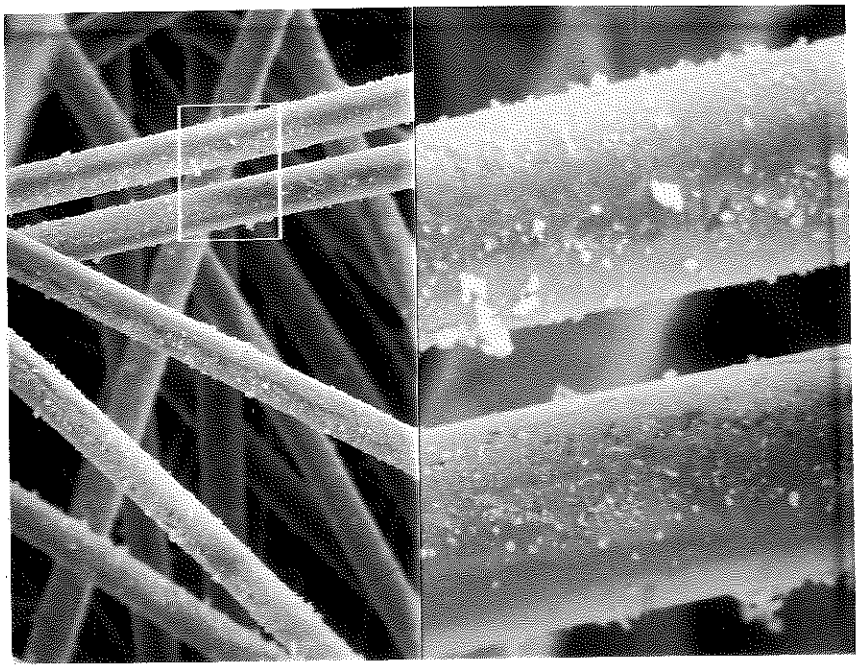

FIGURE 15. TREVIRA 11200
61 DAY, 65 C LEACHATE EXPOSED, SCANNING ELECTRON MICROGRAPH 200/1000x

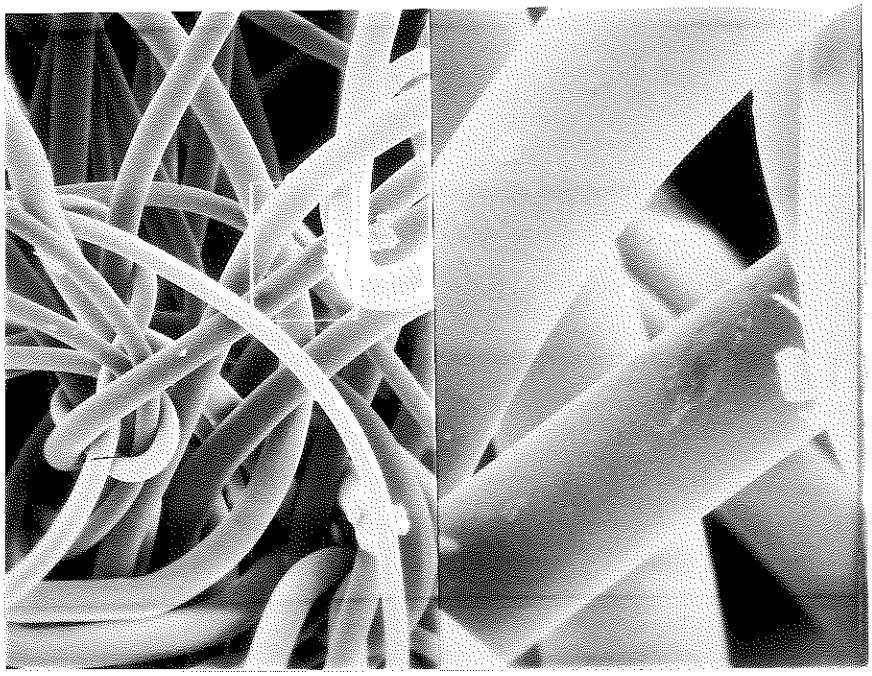

FIGURE 16. TREVIRA 21250
61 DAY, 65 C WATER CONTROL, SCANNING ELECTRON MICROGRAPH, 200/1000x

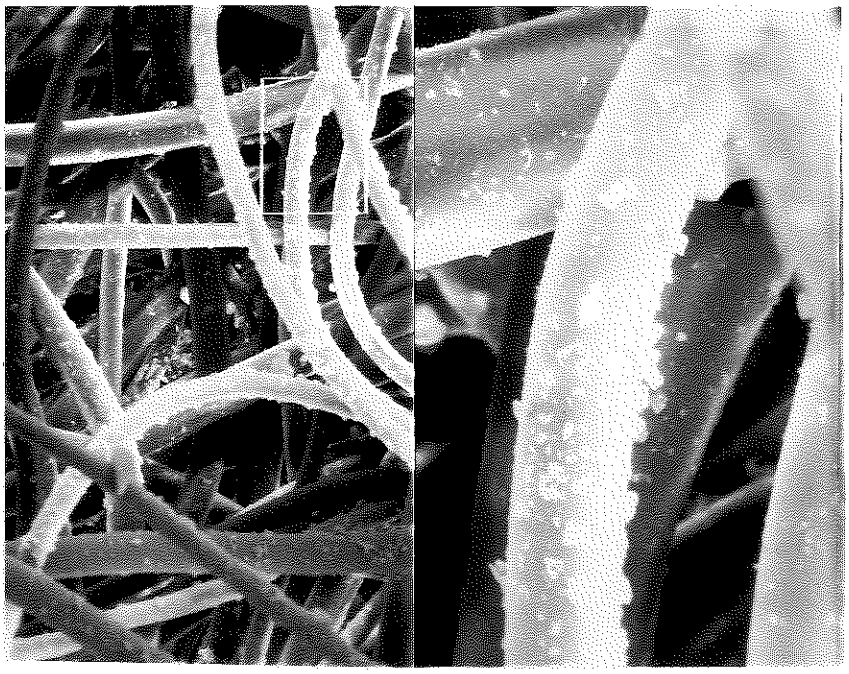

FIGURE 17. TREVIRA 21250
61 DAY, 65 C LEACHATE EXPOSED, SCANNING ELECTRON MICROGRAPH, 200/1000x

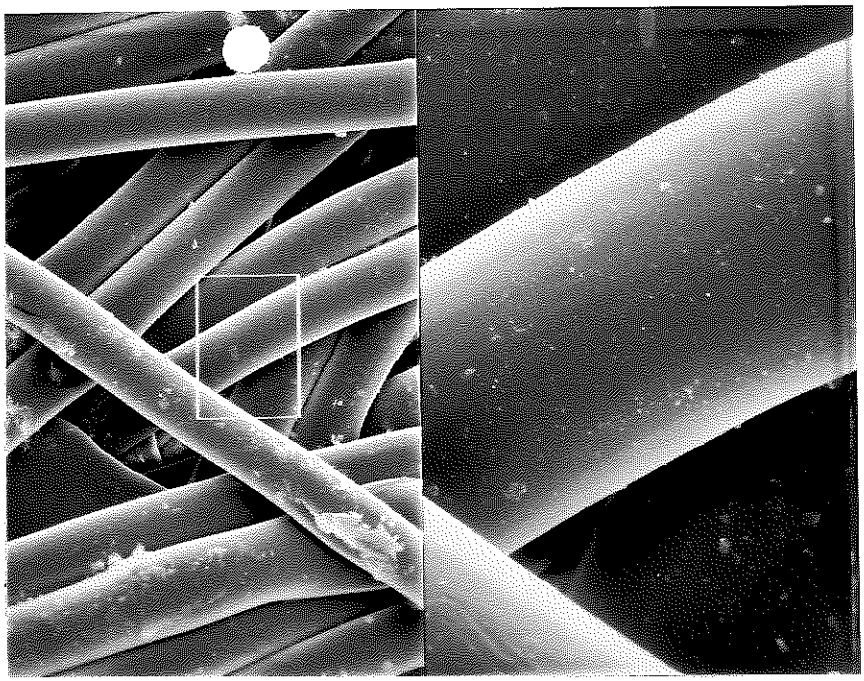

FIGURE 18. TYPAR 3601
61 DAY, 65 C WATER CONTROL, SCANNING ELECTRON MICROGRAPH, 200/1000x

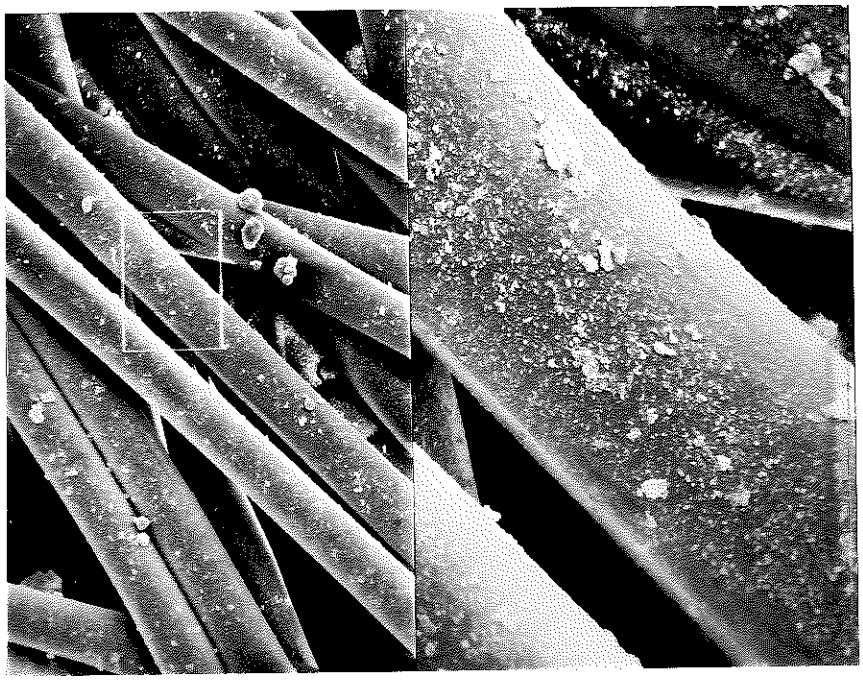

FIGURE 19. TYPAR 3601
61 DAY, 65 C LEACHATE EXPOSED, SCANNING ELECTRON MICROGRAPH, 200/1000x

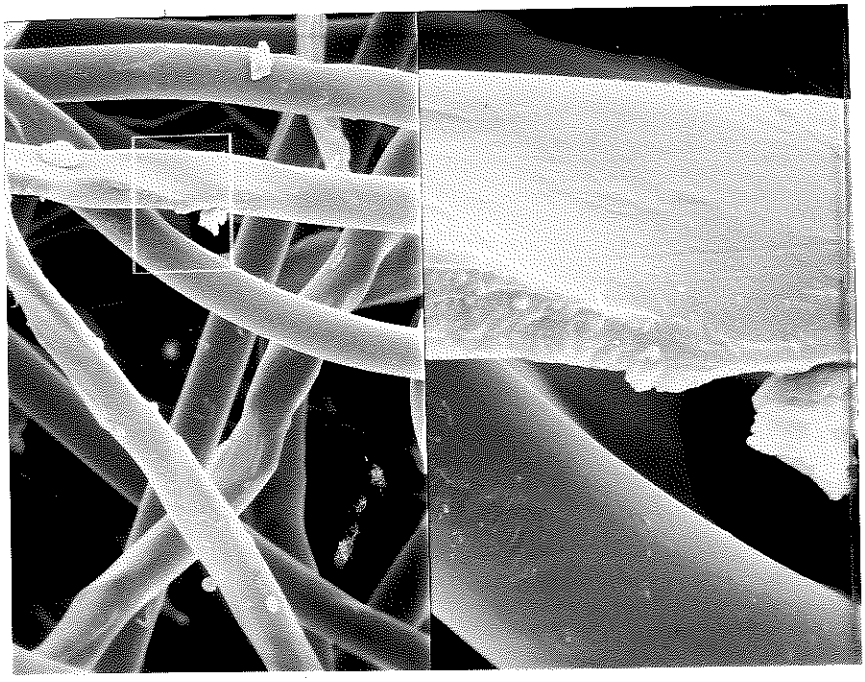

FIGURE 20. FIBRETEX 400
61 DAY, 65 C WATER CONTROL, SCANNING ELECTRON MICROGRAPH, 200/1000x

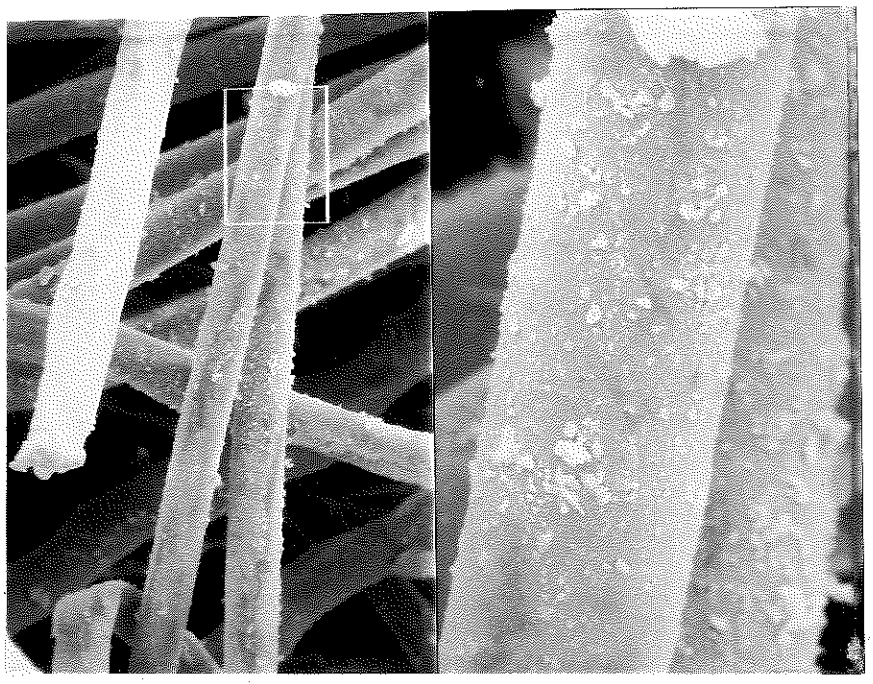

FIGURE 21. FIBRETEX 400
61 DAY, 65 C LEACHATE EXPOSED, SCANNING ELECTRON MICROGRAPH, 200/1000x

no change in the chemical properties of the geotextiles occurred during this time period. The Fibretex 400 showed a slight change in one area of the spectra, but in the opinion of the spectroscopist, did not constitute evidence of any serious degradation. The Typar 3601 also displayed a change in the spectrum in one region, which could not be explained by the spectroscopist. It is thought at this time that this abnormality was indigenous to that particular sample after comparison was made with the 61-day sample.

The second set of 65 C samples was removed at the end of the exposure period, 61 days. When compared with the starting material, once again the Trevira 21250 and Trevira 11200 were comparable. The only changes observed were increases in a band that was determined to be associated with siliceous material (Si-O) such as sand that was adhering to the fibers. There was no change in the basic chemical structure attributed to the polyester fibers. It was therefore concluded that no substantial chemical change had taken place due to the exposure to the leachate at 65 C for 61 days. The Fibretex 400 maintained the slight change in spectrum observed at the 15-day examination and once again was not considered to be evidence of any serious degradation. The Typar 3601, 65 C, 61-day sample did not display the band that was observed in the 15-day sample. The spectrum compared favorably to the control and indicated no chemical degradation.

All four samples once again showed that silicate materials were not being completely removed in the cleaning process. This spectral feature was not related to chemical changes in the sample materials.

In the opinion of the spectroscopist in evaluating the 60-day, 65 C sample spectra, no significant chemical degradation of the geotextile fibers occurred during the exposure period. Samples from the 10 C exposure were not analyzed because no degradation occurred at the higher temperature.

Copies of the starting material and 61-day, 65 C spectra are included in Appendix C.

CONCLUSIONS

Microscopic and macroscopic tests were performed on four geotextile materials that were exposed to leachate generated from sludge obtained at Chemical Waste Management's Vickery, Ohio site. Test specimens were maintained at ~10 C and 65 C to provide baseline and accelerated testing of the geotextile materials. Control samples were also maintained at 65 C while being immersed in distilled water to provide baseline materials for the elevated temperature leachate exposure test. Property comparisons between starting materials, controls, and exposed samples were used to determine whether the Vickery leachate would cause performance-related changes in the geotextile fibers.

The Mullen Burst Test results indicated that no significant loss in material strength occurred in any of the four samples over the course of the exposure period, due to leachate exposure.

The polarized light and scanning electron microscopy evaluations indicate that no physical deterioration of the fibers occurred during the exposure period. Obvious stress or other features observed in any of the fibers were also present in the controls. It is therefore concluded that no significant physical degradation was evident after exposure to Vickery, Ohio, leachate.

The Fourier-Transform Infrared Spectroscopy analysis was intended to indicate if any chemical modification of the polyester or polypropylene fibers was taking place. A comparison of the starting material spectra against the exposed geotextile spectra indicated that the chemical integrity of fibers had not been compromised by the test. The only artifacts observed in the test spectra were indicative of leachate particulates clinging to the fibrous material. It is concluded that none of the sample materials underwent serious chemical degradation during the test period.

There is, therefore, good correlation between the macroscopic, microscopic, and spectroscopic examinations of the geotextile samples. All three of the analytical methods indicate that any of the four geotextile materials should be compatible for a minimum of 25 years with leachate of a type that could potentially be generated at the Vickery, Ohio site.

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Microscopic and macroscopic tests were performed on four geotextile materials that were exposed to leachate generated from sludge obtained at Chemical Waste Management's Vickery, Ohio site. Test specimens were maintained at ~10 C and 65 C to provide baseline and accelerated testing of the geotextile materials. Control samples were also maintained at 65 C while being immersed in distilled water to provide baseline materials for the elevated temperature leachate exposure test. Property comparisons between starting materials, controls, and exposed samples were used to determine whether the Vickery leachate would cause performance-related changes in the geotextile fibers.

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REFERENCES

(1) Physics of Plastics, edited by P. D. Ritchie, Iliffe Books, Ltd., London (1965), "Other Mechanical Properties of High Polymers" (G. Hulse), pp. 152-163.

(2) Mann, Nancy R., Schafer, Ray E., and Singpurwalla, Nozer D., Methods for Statistical Analysis of Reliability and Life Data, John Wiley & Sons, New York (1974).

APPENDIX A

SUMMARY OF U.S. EPA EXTRACTION PROCEDURE AND METHOD 9090

APPENDIX A

EXTRACTION PROCEDURE (EP)[a]

1. A representative sample of the waste to be tested (minimum size, 100 grams) should be obtained using the methods specified in Appendix I or any other methods capable of yielding a representative sample within the meaning of Part 260. (For detailed guidance on conducting the various aspects of the EP, see "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods," SW-846, U.S. Environmental Protection Agency Office of Solid Waste, Washington, D.C. 20460.)

2. The sample should be separated into its component liquid and solid phases using the method described in "Separation Procedure" below. If the solid residue[b] obtained using this method totals less than 0.5% of the original weight of the waste, the residue can be discarded and the operator should treat the liquid phase as the extract and proceed immediately to Step 8.

3. The solid material obtained from the Separation Procedure should be evaluated for its particle size. If the solid material has a surface area per gram of material equal to, or greater than, 3.1 cm^2 or passes through a 9.5 mm (0.375 inch) standard sieve, the operator should proceed to Step 4. If the surface area is smaller or the particle size larger than specified above, the solid material should be prepared for extraction by crushing, cutting, or grinding the material so that it passes through a 9.5 mm (0.375 inch) sieve or, of the material is in a single piece, by subjecting the material to the "Structural Integrity Procedure" described below.

---

a. United States Environmental Protection Agency, 1982, Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods. Second ed., U.S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C. SW-846.

b. The percent solids is determined by drying the filter pad at 80 C until it reaches constant weight and then calculating the percent solids using the following equation: (weight of pad + solid) - (tare weight of pad) x 100 = % solids initial weight of sample.

4. The solid material obtained in Step 3 should be weighed and placed in an extractor with 16 times its weight of deionized water. Do not allow the material to dry prior to weighing. For purposes of this test, an acceptable extractor is one which will impart sufficient agitation to the mixture to not only prevent stratification of the sample and extraction fluid but also ensure that all sample surfaces are continuously brought into contact with well mixed extraction fluid.

5. After the solid material and deionized water are placed in the extractor, the operator should begin agitation and measure the pH of the solution in the extractor. If the pH is greater than 5.0, the pH of the solution should be decreased to 5.0 $\pm$ 0.2 by adding 0.5N acetic acid. If the pH is equal to or less than 5.0, no acetic acid should be added. The pH of the solution should be monitored, as described below, during the course of the extraction and if the pH rises above 5.2, 0.5N acetic acid should be added to bring the pH down to 5.0 $\pm$ 0.2. However, in no event shall the aggregate amount of acid added to the solution exceed 4 ml of acid per gram of solid. The mixture should be agitated for 24 hours and maintained at 20 to 40 C (68 to 104 F) during this time. It is recommended that the operator monitor and adjust the pH during the course of the extraction with a device such as the Type 45-A pH Controller manufactured by Chemtrix, Inc., Hillsboro, Oregon 97123 or its equivalent, in conjunction with a metering pump and reservoir of 0.5N acetic acid. If such a system is not available, the following manual procedure shall be employed:

(a) A pH meter should be calibrated in accordance with the manufacturer's specifications.

(b) The pH of the solution should be checked and, if necessary, 0.5N acetic acid should be manually added to the extractor until the pH reaches 5.0 $\pm$ 0.2. The pH of the solution should be adjusted at 15-, 30-, and 60-minute intervals, moving to the next longer interval if the pH does not have to be adjusted more than 0.5N pH units.

(c) The adjustment procedure should be continued for at least 6 hours.

(d) If, at the end of the 24-hour extraction period, the pH of the solution is not below 5.2 and the maximum amount of acid (4 ml per gram of solids) has not been added, the pH should be adjusted to 5.0 + 0.2 and the extraction continued for an additional four hours, during which the pH should be adjusted at 1-hour intervals.

6. At the end of the 24-hour extraction period, deionized water should be added to the extractor in an amount determined by the following equation:

$V = (20)(W)-16(W)-A$

V = ml deionized water to be added

W = weight in grams of solid charged to extractor

A = ml of 0.5N acetic acid added during extraction.

7. The material in the extractor should be separated into its component liquid and solid phases as described under "Separation Procedure."

8. The liquids resulting from Steps 2 and 7 should be combined. This combined liquid (or the waste itself if it has less than 1/2 percent solids, as noted in Step 2) is the extract and should be analyzed for the presence of any of the contaminants specified in Table 1 of 261.24 using the Analytical Procedures designated below.

SUMMARY OF U.S. EPA METHOD 9090

Method 9090 is an experimental procedure to determine long-term compatibility of liner material exposed to leachate for a period of 120 days at one elevated temperature. To measure this compatibility, physical properties of the liner material are tested before and after the liner has been exposed to the leachate. The results should provide an estimate of the properties of the liner material at the time of site closure. The method is described below.

Use an exposure tank large enough to contain liner specimen samples and to support the samples so they do not touch the tank's bottom or sides. Maintain the tank temperature at 50 ± 2 C. Equip the tank with the means to prevent evaporation of the solution (e.g., cover equipped with a reflux condenser).

To obtain a representative sample, conduct sample collection, sample preservation, and leachate handling in accordance with Code of Federal Regulations 254.221(a) and (c), 264.228(a), 264.251(a), 264.252, and 264.253, 264.301(a) and 264.310(a).

Perform the following tests on unexposed samples of the HDPE.

1. Tear resistance, machine and transverse directions, five specimens each direction for nonreinforced liner materials only
2. Puncture resistance, five specimens, FTMS 101B, Method 2065
3. Tensile properties, machine and transverse directions, five tensile specimens each direction
4. Hardness, Duro A (Duro D if Duro A reading is greater than 80), ASTM D2240
5. Elongation at break, to be performed only on membrane material that does not have a fabric or other nonelastomeric support on its reverse (away-from-waste) face.

Cut the liner material to fit the sample holders and cut enough samples to have at least three samples for each waste and each exposure period. Measure these samples for the following characteristics:

- Gage thickness, mil or mm, average of the four corners
- Mass, g, to one-hundredth of a gram.

- o Length, cm, average of the lengths of the two sides.
- o Width, cm, average of the widths of the two ends.

At the end of 30, 60, 90, and 120 days of exposure, remove enough samples from the leachate to determine the membrane's physical properties. Cool the wet specimen in a labeled container of fresh leachate at room temperature for 1 hour before testing. Wipe off the specimen to remove as much waste material as possible, rinse it well with water, and place it in a labeled polyethylene bag to prevent the specimen from drying out. Test the sample within 24 hours of removal from the exposure tank.

To test the immersed sample, wipe off any remaining waste and rinse the sample with deionized water. Blot the specimen dry and measure its thickness, mass, length, and width.

Perform tests 1 through 4 listed above on the exposed specimen to determine any changes in the liner material after exposure to the leachate. Plot the results on a curve for each property over the time period of 0 to 120 days.

APPENDIX B

CLEANING PROCEDURE FOR GEOTEXTILE SAMPLES

APPENDIX B

Cleaning Procedure for Geotextile Samples

The following procedure is to be used for the cleaning of geotextile samples in preparation for their analysis:

1. Remove samples from leachate, being careful to handle them only by the outer edges. We do not want to crush or damage in any way the portions of the samples that are actually going to be analyzed. If samples are being pulled from the elevated temperature baths, allow samples to cool to room temperature in a container of leachate before cleaning.

2. Allow geotextile material to drip-dry and then gently rinse the sample with deionized water to remove the bulk of the leachateand any solid material.

3. Place the sample into an ultrasonic bath containing 200-proof ethanol. Bathing time should take approximately 3 minutes. If a longer period is needed to do a thorough cleaning, please note. Change the ethanol in the bath when the solvent appears dirty.

4. Remove the sample from the ultrasonic bath and allow to drip-dry.

5. Rinse the sample again with a gentle stream of deionized water to displace the solvent and remove any lingering leachate. Allow to drip-dry until most of the water has drained from the sample.

6. Place the geotextile sample in a vacuum oven and heat at approximately 100 F with maximum vacuum for 1 hour. Check to see if sample is dry. If longer drying time is needed, please note.

7. Remove dried samples from oven and place geotextile material into a properly labeled plastic bag for storage. Samples are then ready for analysis.

   Before and during the cleaning operation, note any observed changes in the geotextile materials which could be indicators of degradation of the samples.

   Also, any baseline samples should also be submitted to the same cleaning procedure before being sent to analysis.

APPENDIX C

FOURIER-TRANSFORM INFRARED SPECTRA

APPENDIX C

FOURIER-TRANSFORM INFRARED SPECTRA

Fourier-Transform Infrared Spectra comparing the starting geotextile material with that of the samples exposed to leachate for 61 days at 65 C.

In order to be able to evaluate the enclosed spectra, the following information is being supplied. The basic structure of the molecules has been illustrated and the major components of the spectrum and where the bands (or peaks) are to be found is included. The wavenumber values are found at the bottom of the spectrum and range from 3000 to 700 going from left to right.

When comparing the spectra, if one looks at the starting material printout and the leachate exposed printout and if a good match results, then it is assumed chemical degradation has not occurred.

(1) Trevira Samples

Polyester

$$[CH_2-\overset{\overset{O}{\|}}{C}-O-CH_3]_X$$

Wavenumber	Chemical Structure
3000-2800 region	C-H bonds
1720	C=O bonds
1240	C-O bond
1150-1100 region	O-CH_3 bond

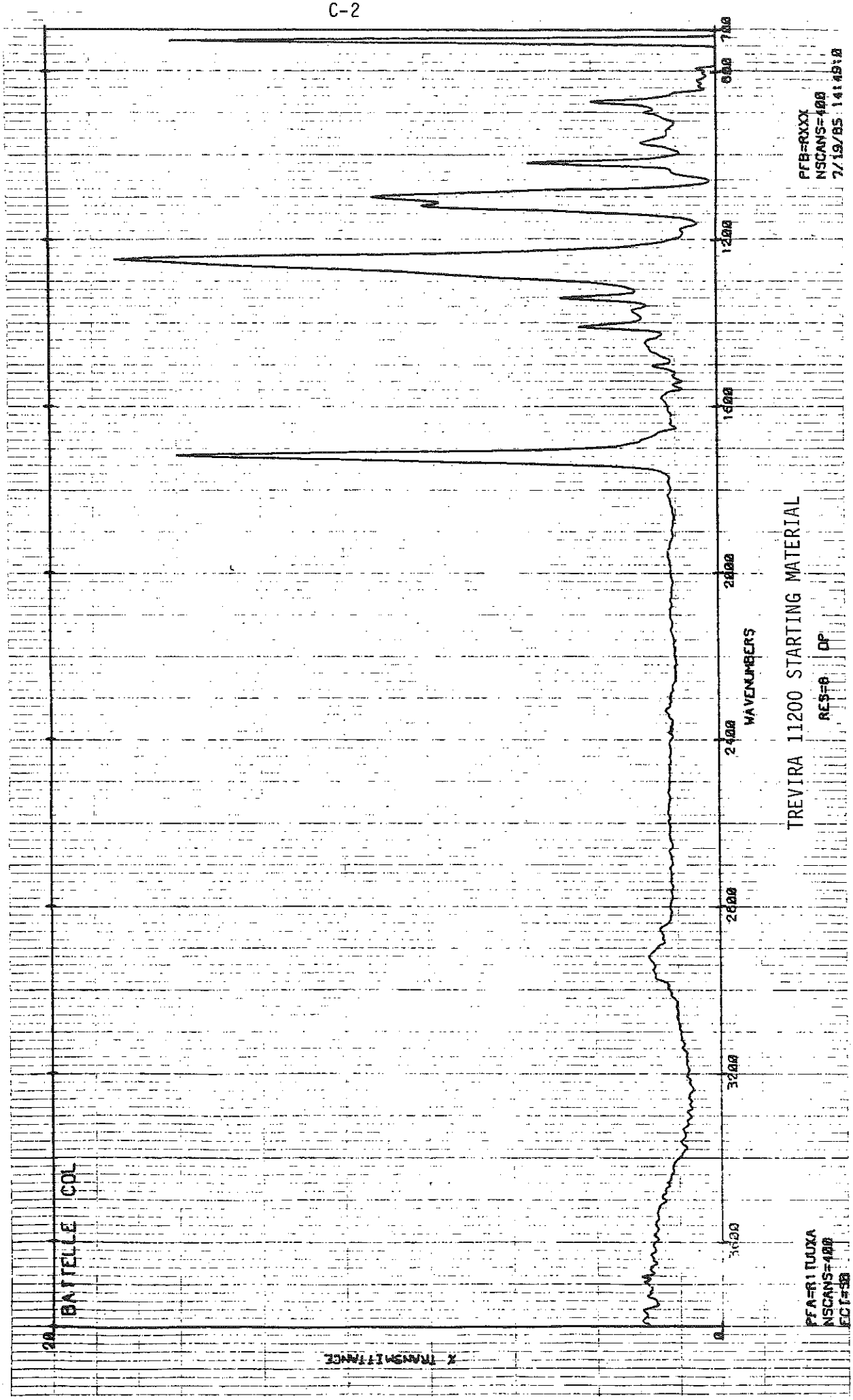
(2) Typar and Fibretex Samples

Polypropylene

$$[CH_2 = CH - CH_3]_X$$

Wavenumber	Chemical Structure
3000-2800 region	C-H bonds
1650	C=C bond
1460-1380 region	CH_2 bonds

Large band located at approximately 1100 wavenumbers is an Si-O bond associated with siliceous material (sand) from the sludge. This is from foreign particles adhering to the fiber mat and does not indicate chemical degradation.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WAVENUMBERS
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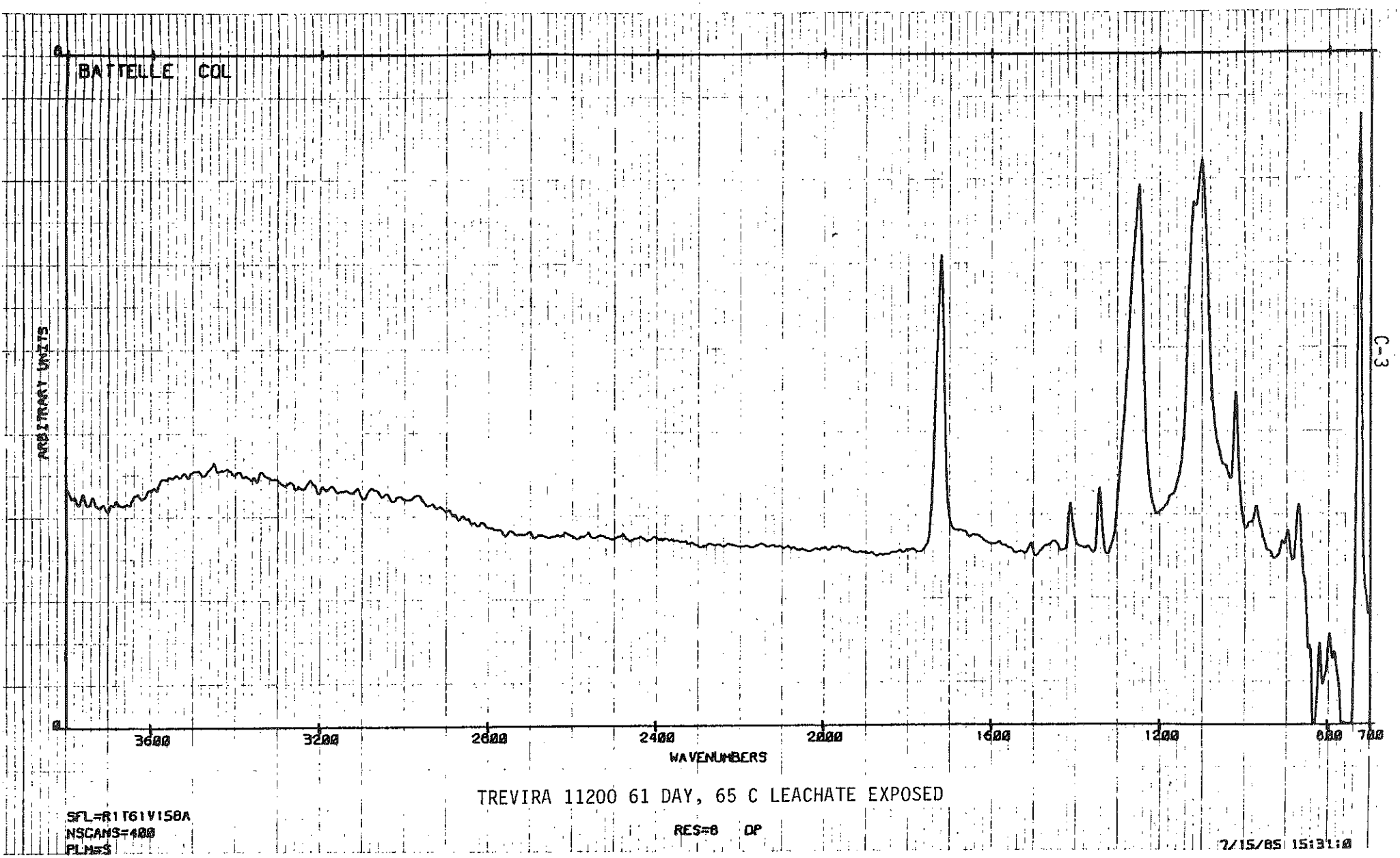
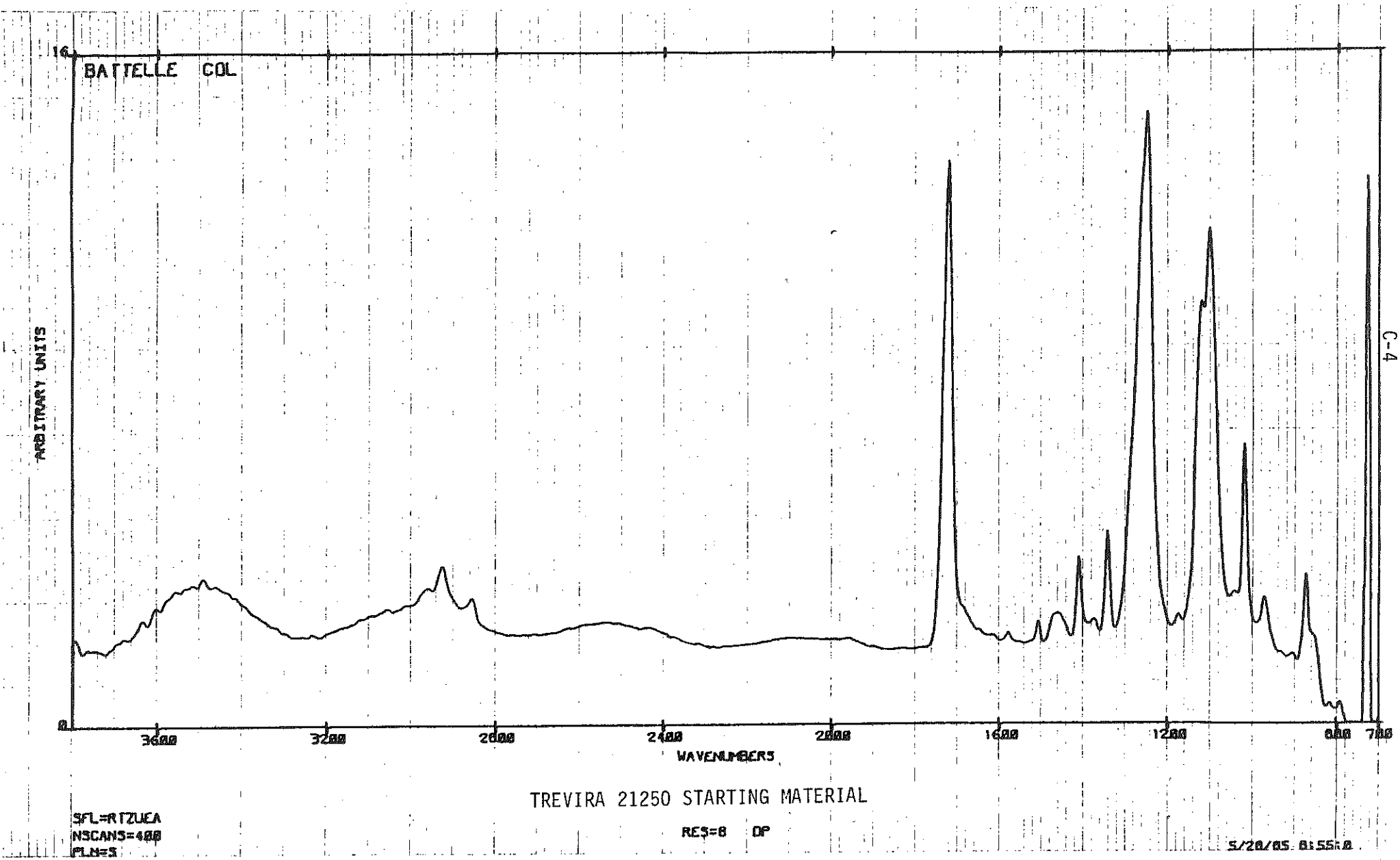
NSCANS=400



TREVIRA 11200 61 DAY, 65 C LEACHATE EXPOSED

09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3200
2800
2400
2000
1600
1200
800
700
WAVENUMBERS
C-4
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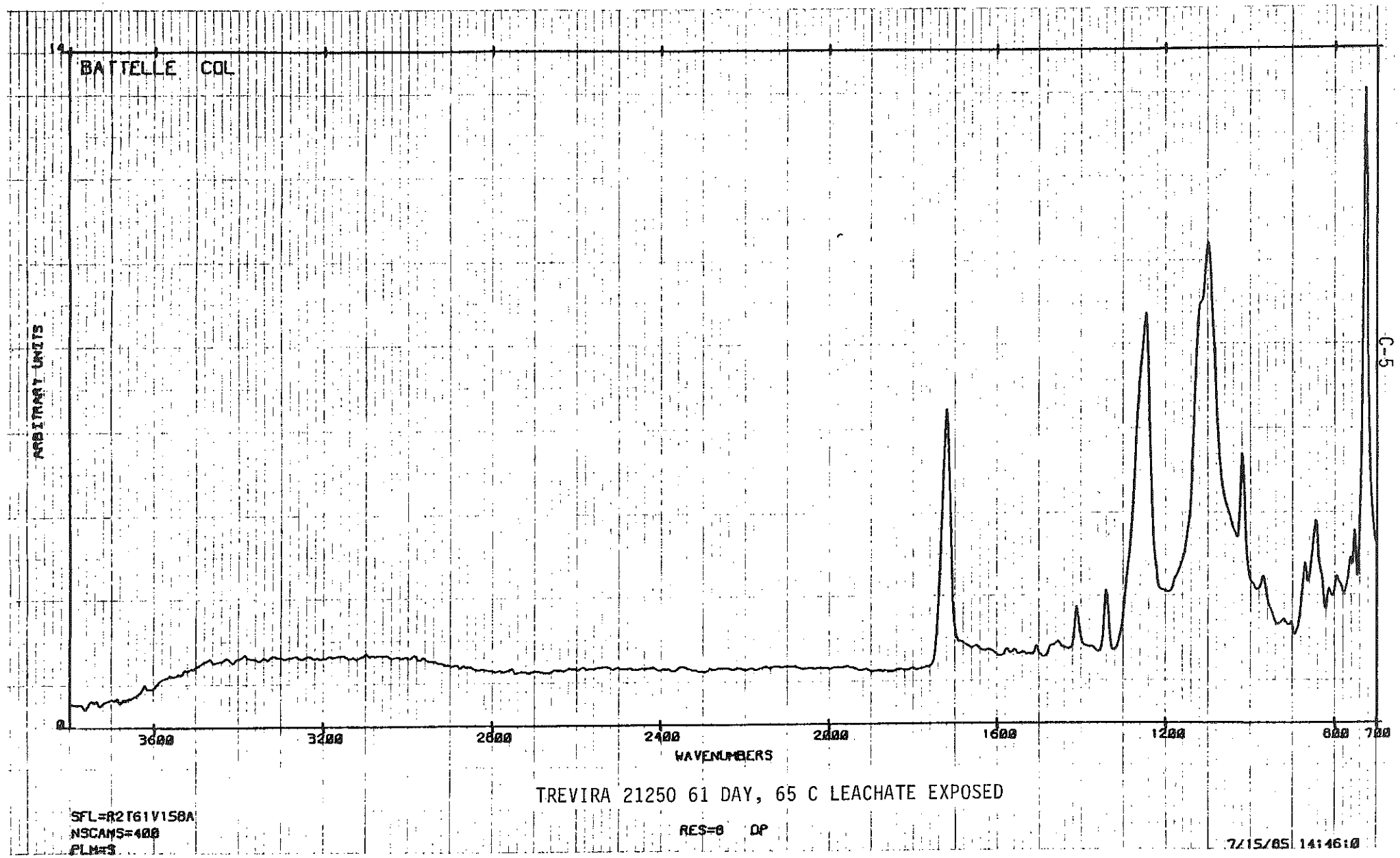
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ARBITRARY UNITS
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3600
3200
2800
2400
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1200
800
700
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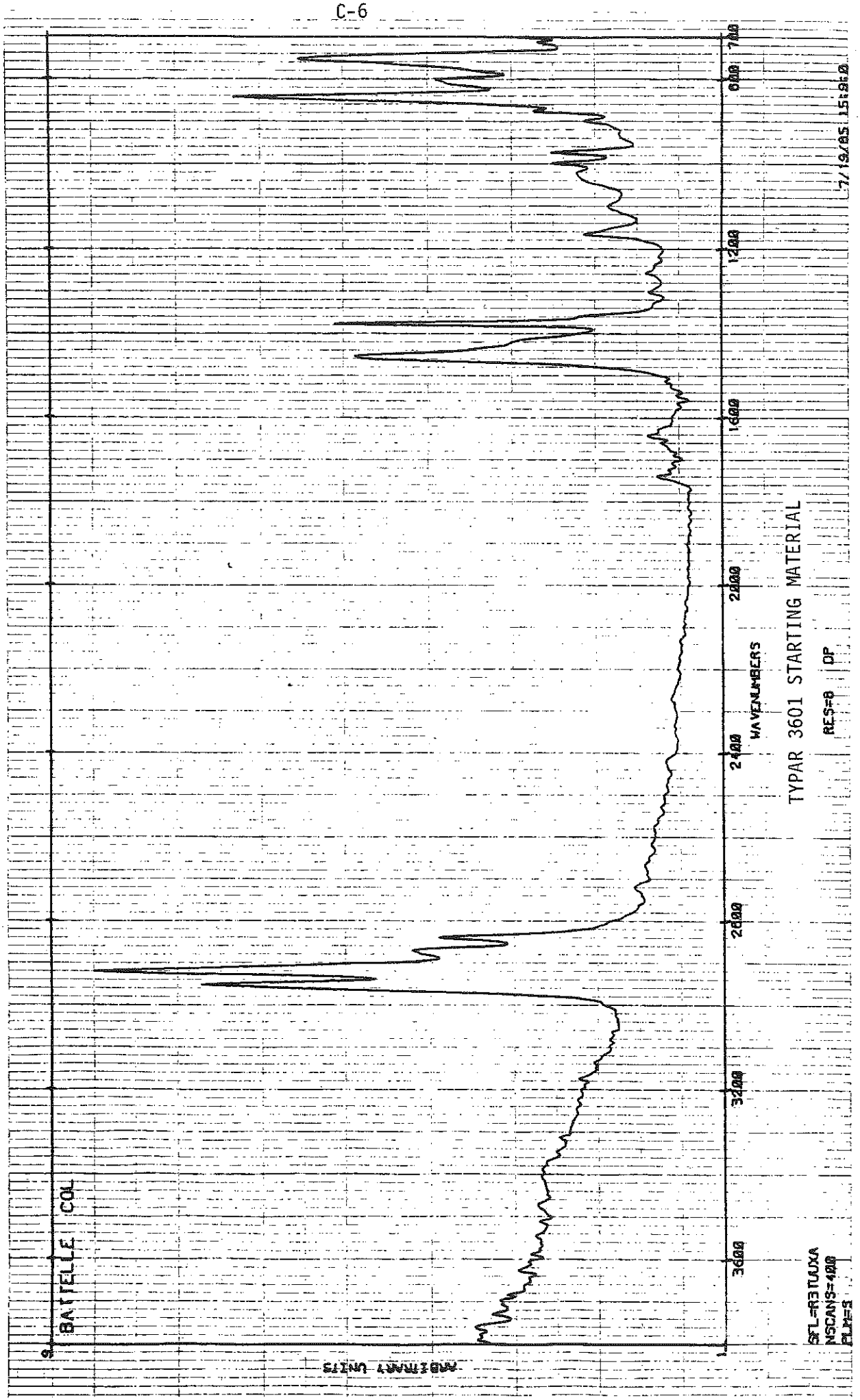
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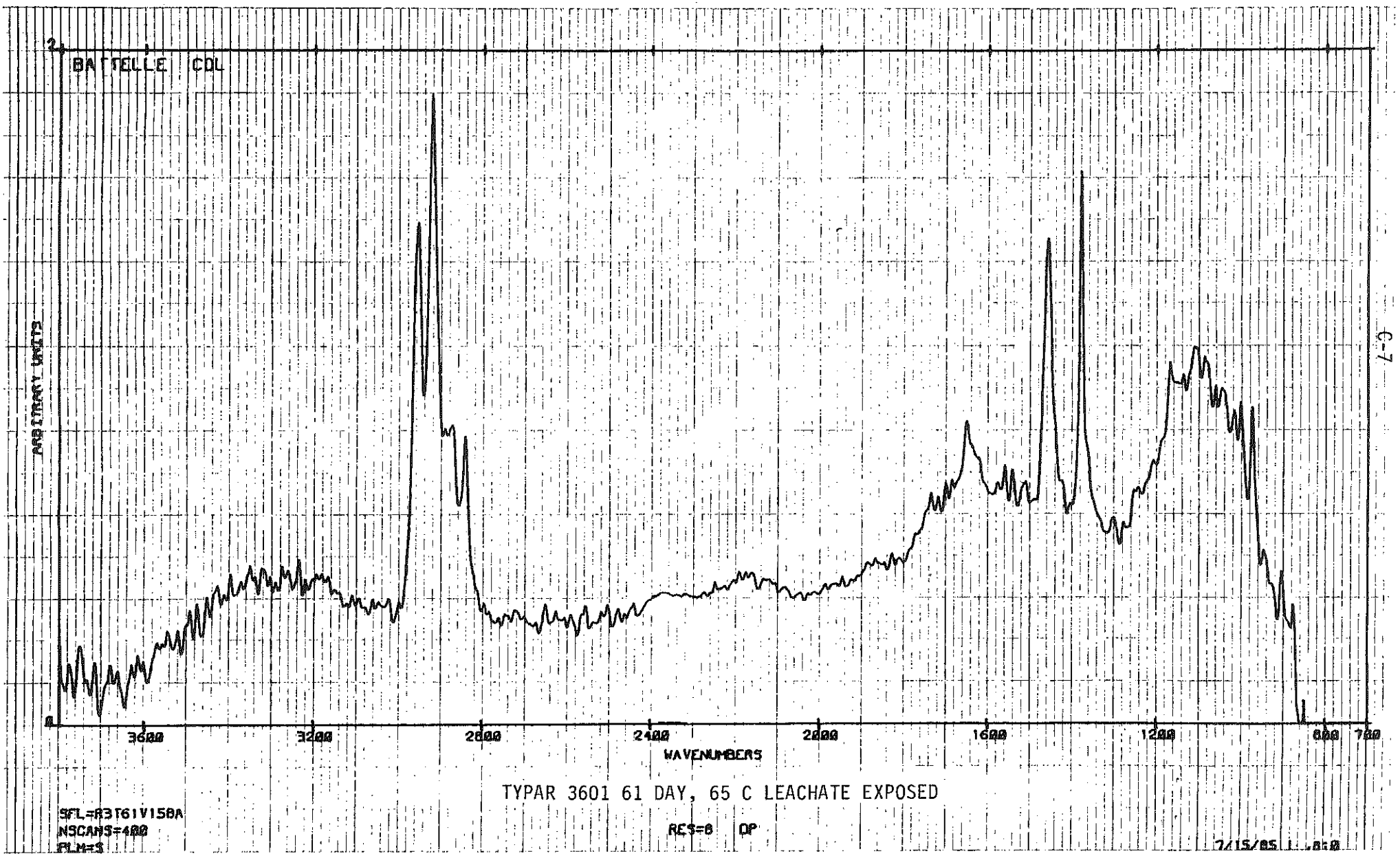
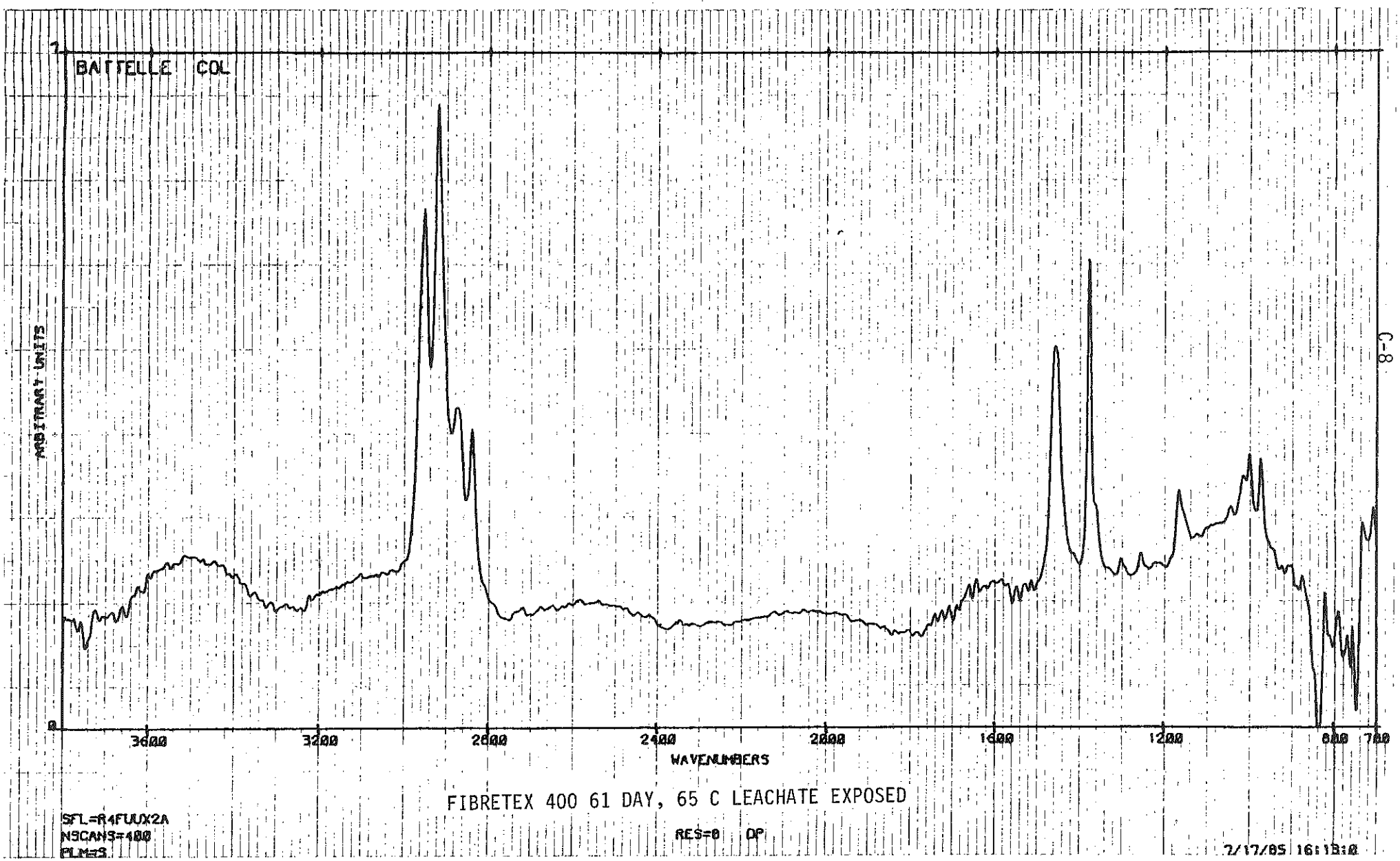
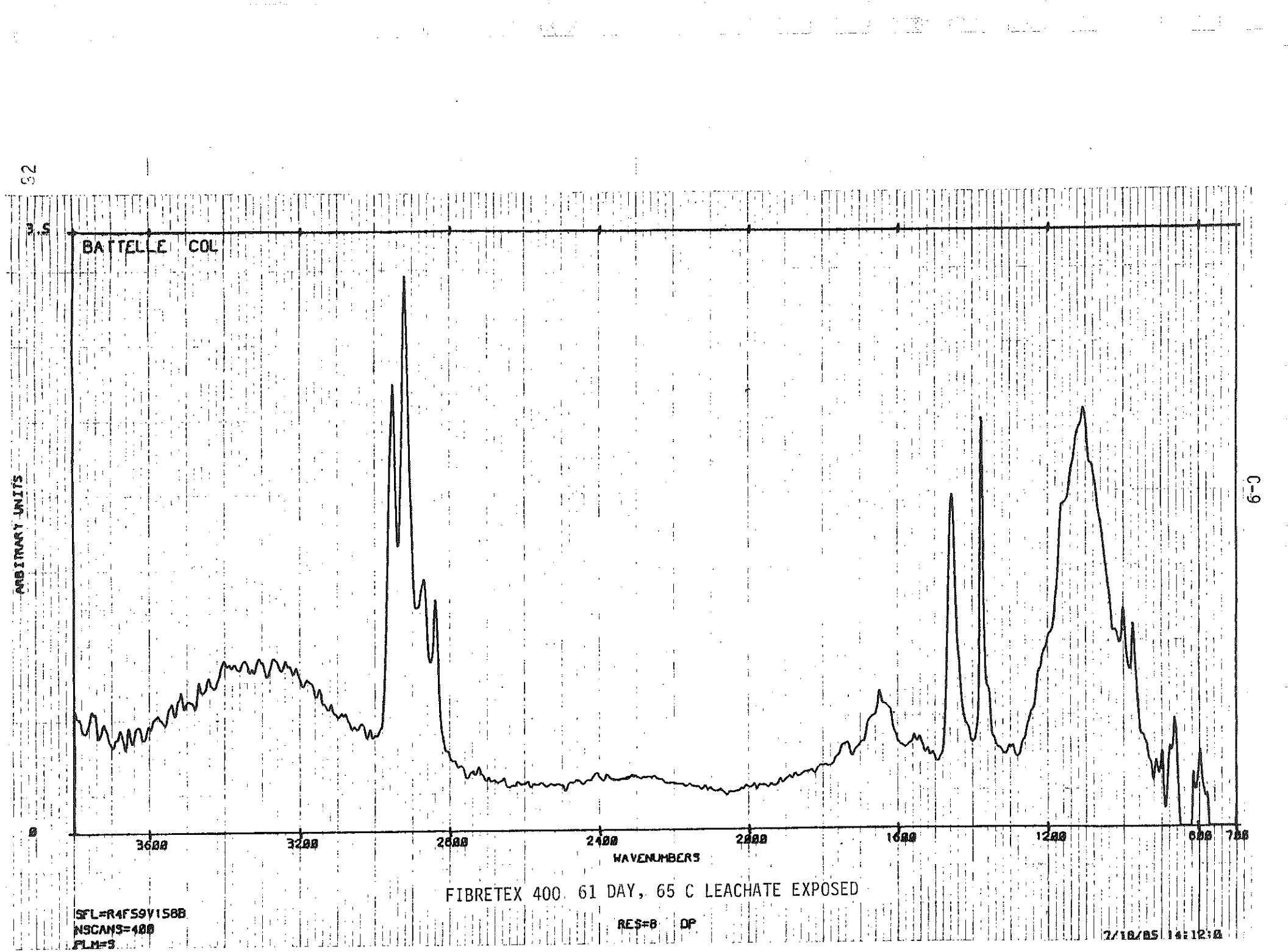


TYPAR 3601 61 DAY, 65 C LEACHATE EXPOSED



FIBRETEX 400 61 DAY, 65 C LEACHATE EXPOSED

C-8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FINAL REPORT

on

ASSESSMENT OF LINER COMPATIBILITY WITH LEACHATE EXTRACTED FROM VICKERY (OHIO) SLUDGE

to

CHEMICAL WASTE MANAGEMENT, INC.

May 14, 1985

by

B. W. Vigon, S. L. Clark, R. E. Thomas,
J. P. Pfau, and R. E. Sharpe

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

EXECUTIVE SUMMARY

Chemical Waste Management, Inc., has contracted with Battelle's Columbus Laboratories to implement the EPA liner compatibility testing methodology for estimating the potential effect of Vickery leachates on high-density polyethylene (HDPE) liner material to be used for lining the on-site closure cell in which chemically-fixed sludges are to be placed. The leachate tested was generated using a modified EPA extraction procedure (EP) applied to the unfixed sludge. This represents a worst case because the fixed sludge will retain more of the contaminants. Tests of liner properties are required to demonstrate long-term compatibility with landfill leachates.

To show the suitability of HDPE liner material for use at Chemical Waste Management's Vickery, Ohio, facility, the liner material was exposed to the representative leachate generated from sludge collected at the Vickery Facility. Exposure of high-density polyethylene (HDPE) liner specimens by submersion in leachate tanks was in conformance with the procedures specified by U.S. EPA Method 9090. This test was more rigorous than that called for by Method 9090 in that two additional temperatures were used instead of only the one (50 C) specified in Method 9090. The testing at 80 C provided a more severe exposure environment than that called for by the EPA. After nominal intervals of 30, 60, 90, and 120 days, between 5 and 15 appropriately configured liner specimens at each test temperature were removed from the exposure tanks. These liner specimens were measured to evaluate physical changes as measured by tensile properties, absorption/leaching, and puncture properties that may have occurred during the testing period. The tensile tests involved taking a group of specimens of liner material that had been exposed to the leachate and applying tensile stress (by pulling on the ends of the test specimens). Three sets of measurements were made: (1) tensile strength at the breaking point of the material, (2) tensile strength at the yield point of the material, and (3) the percentage elongation at the breaking point. This latter test is a measure of the plasticity of the material.

The puncture tests paralleled the tensile tests. Three sets of measurements were made: (1) puncture strength at the breaking point of the material, (2) puncture point at the yield point of the material, and (3) the percentage elongation at the breaking point. In both the tensile and puncture property tests, the results from leachate exposed specimens were compared to the test results from unexposed control specimens. This procedure accounts for the uncertainties in test method and the normal manufacturing variation in the HDPE liner material itself.

Finally, the sorption/leaching tests were designed to measure weight gained due to moisture or chemical migration into the polymer matrix or weight loss due to extraction of materials such as plasticizers from the material.

The test results showed no evidence of significant deterioration of the liner specimens at the end of any period up to and including 120 days of exposure to the Vickery leachate at 13 and 50 C. The 80 C test data indicated a significant loss of plasticity as measured by percentage tensile elongation at break. However, the other tests indicate that this change did not affect the tensile or puncture strength properties of the liner. The statistical analyses showed little change in tensile properties and a general improvement in puncture properties, relative to the controls, at all temperatures. The sorption tests resulted in weight change values well below the 10 percent needed to cause significant change in liner properties. None of the tests indicated a degradation of properties over the 120-day test period.

Based on the 50 C tests and accepted U.S. EPA guidelines concerning their interpretation, it is concluded that the HDPE liner material tested will be compatible for a minimum of 25 years with leachate of the type that could be potentially generated from the Vickery facility. Furthermore, the test results under the more severe exposure conditions at 80 C indicate that the liner should last well in excess of 25 years.

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FINAL REPORT

on

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May 14, 1985

INTRODUCTION

Chemical Waste Management, Inc. is preparing a closure plan for their facility at Vickery, Ohio. A key element in this plan is the chemical fixation of sludge contained in a number of large lagoons. After reacting the sludge with selected fixation reagents, the mixture will be removed from the lagoons to allow the construction of an engineered closure cell (landfill). The bottom of the closure cell will be lined with a high-density polyethylene (HDPE) material. (For the purposes of this test program, an HDPE material manufactured by Gundle Liner Systems was used as representative of commercial HDPE.) The fixed sludge material will then be placed into the engineered closure cell, and the cell will be sealed.

The U.S. Environmental Protection Agency requires the laboratory testing of HDPE liner material to determine its compatibility with leachate. EPA Method 9090 involves testing at an elevated temperature of 50 C to produce

exposure conditions which accelerate the actual exposure time to that expected in 25 years of field exposure at ambient temperature. In this testing program for the Vickery site, the requirements of Method 9090 were met by running some of the exposure tests at the required 50 C temperature. In addition, a set of tests was run at 80 C to establish the compatibility of the leachate and liner under even more severe conditions than are currently required by the EPA. Liner compatibility was tested with both acidic (pH2) and neutral (pH7) leachates at the 80 C temperature.

There is currently no leachate being generated or collected at the site so a liquid leachate was generated from unfixed sludge using a modification of the EPA Extraction Procedure (EP) test. Since the actual sludge to be disposed of in the closure cells will be chemically fixed, testing with leachate generated from the unfixed material should be conservative with respect to the leaching potential of the actual material placed in the closure cell.

The following sections describe the methodology for generating and testing the leachate, the results of the physical property tests conducted on the liner specimens, and the conclusions based on those tests for liner longevity.

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* B. W. Vigon and F. L. DeRoos. 1984. Assessment of Waste Sludge Stabilization Alternatives. Report from Battelle Columbus Laboratories to Chemical Waste Management, Inc.

METHODOLOGY AND MATERIALS

This study was conducted using EPA-approved protocols (Method 9090) to the extent possible. However, the testing of liner compatibility is a developing one, and the procedures are evolving so that some modifications have been made. The chemical analysis of the sludge and EP leachate for heavy metals and specific organic chemicals was reported previously* and is not repeated here for the sake of conciseness.

EP Leachate Generation

Approximately 20 gallons of leachate were required for these tests. The standard EP test setup employs a tumbling extractor to generate the relatively small quantities (less than a liter) of leachate needed for chemical analyses. The procedure was scaled up in this case to produce enough leachate for the exposure tanks by substituting a 5-gallon container and a motor-driven paddle stirrer for the tumbler extractor. The paddle stirrer was set at a high enough speed to keep the slurry in suspension at all times as required by the EPA test method. Except for the stirrer drive shaft hole, the top of the extraction container was sealed to prevent loss of volatile components. Small amounts of the volatile components were lost when the headspace air above the liquid suspension was disturbed during the addition of dilution water, but in comparison with the amount of these materials contained in the sludge, these minor losses were inconsequential.

Each of the four batches of leachate was obtained from 933.5 grams of "as-received" sludge to which 15 liters of Barnstead deionized water was added. The pH of the mixed suspension was measured initially with a pH meter calibrated at 4.0 and 7.0. Batch 1 had a measured pH of 1.73 and Batch 2 measured 1.64 so there was no need to add supplemental acetic acid as called for in the procedure when the pH is greater than 5. The extracts were stirred for 24 hours at the end of which time the pH values were 1.89 and 2.00, respectively. Deionized dilution water was added as indicated in the procedure to give a final volume of 19.785 liters (5 gallons) in each container. The neutralized leachate sample was prepared by adding approximately 100 ml of

a concentrated (ION) caustic soda solution. Filling the containers to the top minimized the further losses of volatile components to the headspace in the containers. The leachate container was sealed and the particulate material allowed to settle at 4 C until the exposure tests were initiated.

The liquid supernatant portion of the EP leachate was used for the exposure tests described below.

Exposure Test Methodology

The general experimental conditions selected for exposing HDPE liner material to Vickery leachate are based on a knowledge of the characteristics of the liner material, on the need for statistically valid results, and on a theoretical form of the mathematical functions that describe the liner degradation.

Accelerated testing depends on elevated stress. In this case, temperature was used as the stress variable. The intermediate temperature used (50 C) is the one required by Method 9090, but an additional higher stress test was done at 80 C.

In addition, specimens were also exposed at the lowest expected temperature in the closure cell (13 C). This temperature was selected as representative of the minimum temperature to which the liner would be exposed on a sustained, long-term basis. It is the expected subsurface temperature at depths not affected by ambient above-ground temperatures. In actual field service, portions of the liner could experience lower temperature on an intermittent basis at shallower depths. The 13 C test data provided a baseline control for the statistical analyses.

The other general requirement for the experiments is that there be no systematic assignment of experimental equipment or specimens in the performance of the program. That is, the first exposure tank constructed should not be assigned to the highest temperature, etc. To satisfy this requirement, all equipment assignment was randomized, as was the selection and placement of individual specimens in the exposure tanks and the selection of specimens for evaluation at the end of each time period.

Development of the Tank

Each exposure tank consisted of a 3-gallon Pyrex glass chromatography jar containing a Xylan-coated stainless steel wire rack for suspending the HDPE liner test specimens in the Vickery leachate. The wire rack was engineered to prevent contact between individual test specimens and their contact with the bottom and sides of the glass jar and still allow circulation of leachate. Each exposure tank held approximately 108 liner test specimens. Each exposure tank was capped with a 0.125-inch thick neoprene rubber gasket lid to help prevent evaporation losses. The neoprene rubber was used because of its good chemical resistance and its low Durometer value of 40. The 80 C testing conducted subsequent to the 50 C testing used an aluminum plate to add stiffness to the top cover and to allow more uniform screw tension. The exposure tank lids also contained inlet ports for cold fingers, for the shafts of Xylan-coated 120 volt, 60 rpm electric motor-driven paddle stirrers, and for the cases of thermocouple temperature monitors. The elevated-temperature tanks (EC 35, 37, and 38) were maintained at the required elevated temperatures of 50 and 80 C through the use of heating tape, aluminum-baked fiberglass insulation, and temperature controllers. The temperature of the ambient temperature tank (EC 36) was maintained by immersing the tank in an ice bath to keep the tank at 13 C and by using fiberglass insulation and temperature controllers. Figure 1 shows an exposure tank and the components before assembly, and Figure 2 shows an assembled tank.

Testing HDPE Liner for Puncture, Tensile Strength, and Absorption/Leaching After Exposure to Vickery Leachate

Each exposure tank at each temperature contained enough samples to collect data at intervals of 30, 60, 90, and 120 days. Each tank contained 36 puncture samples, 36 tensile samples, and 36 absorption samples. The samples used for this test program were cut from a sheet of Gundle HDPE liner material supplied by Gundle Lining Systems, Inc., Houston, Texas.

Figure 1

Exposure Tank and Components Before Assembly

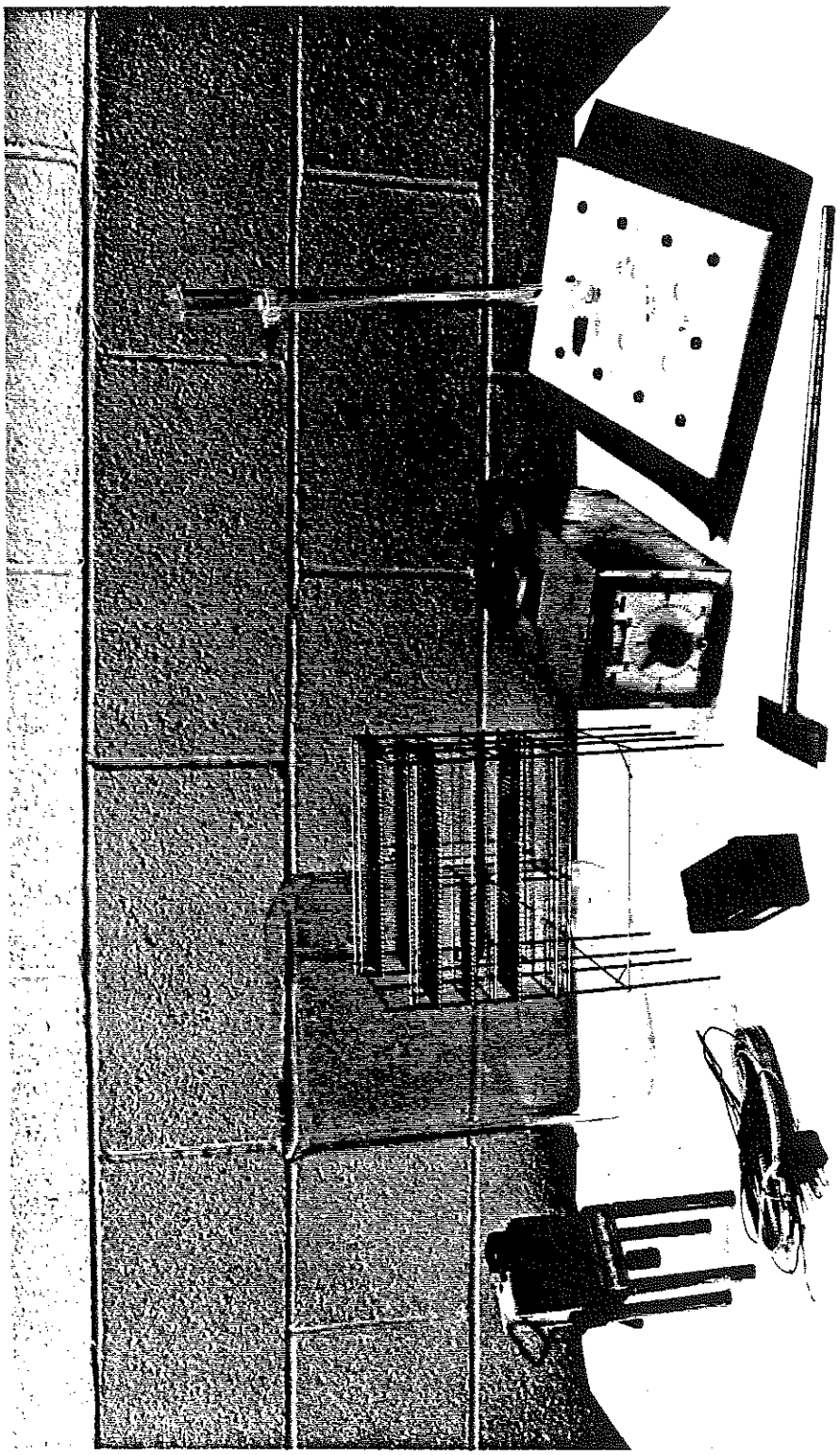
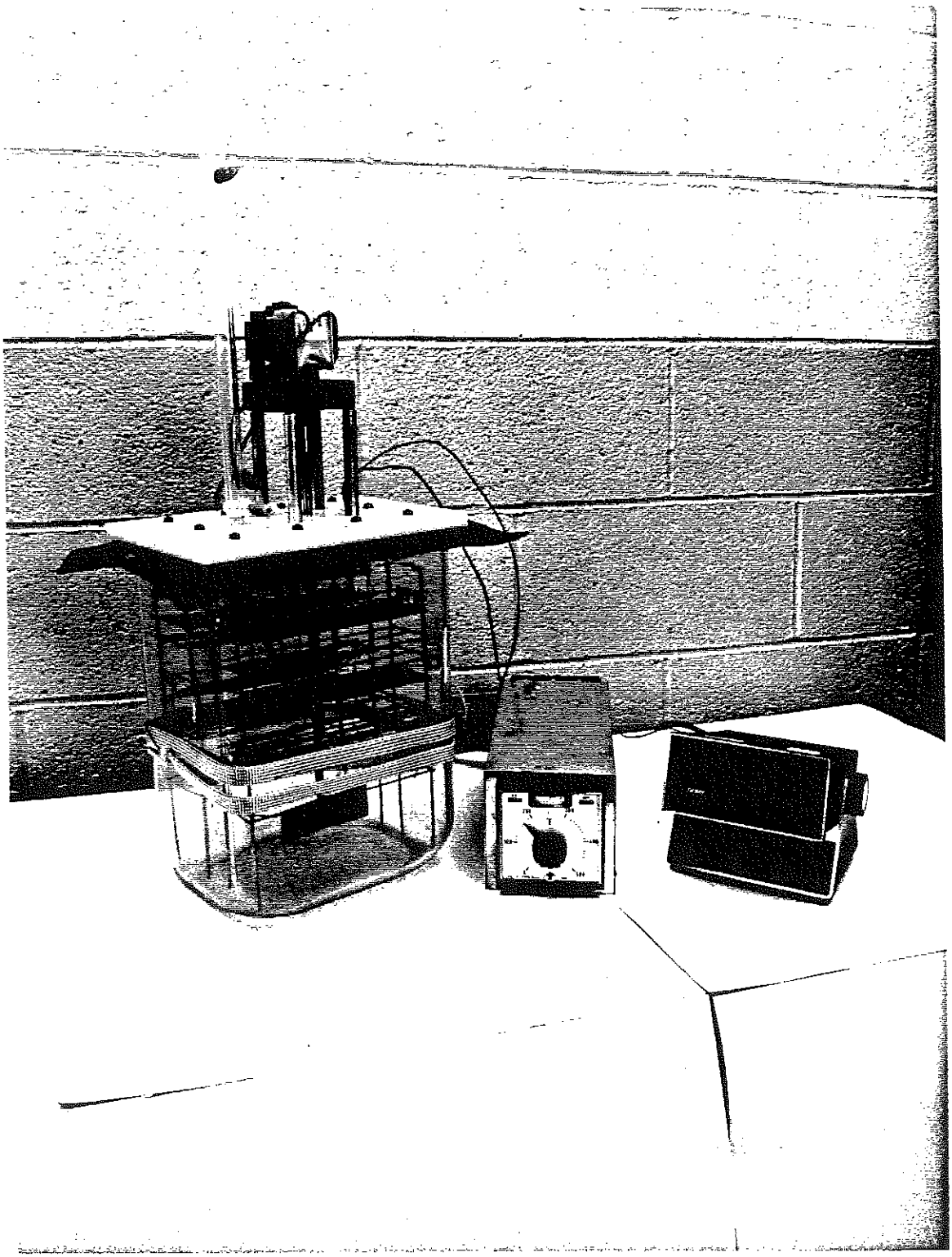


Figure 2

Assembled Exposure Tank



Geometry of Test Specimens

The geometry and dimensions of the tensile and puncture test specimens were measured in accordance with EPA Method 9090 with slight modifications in the procedure (Figure 3). Tensile specimens were die cut into standard "dog bone" shape dimensions. The dimensions of the tensile specimens were determined by cutting 100 specimens, measuring them with a micrometer, and averaging the results to obtain the dimensional measurements of a "standard" sample. The resulting average "standard" sample dimensions were then used for the tensile property calculations (Table 1).

The puncture samples were shear cut to dimensions 2 inches square. The only required dimension of puncture test specimens was thickness. The average thickness obtained for the 100 tensile specimens was used as the average thickness of the puncture specimens.

The absorption test specimens were also shear cut to dimensions 1 inch by 2 inches. The width, length, and weight (mass) of each absorption/leaching test specimen were recorded prior to placement in the exposure tank. A Mettler analytical balance was used to determine sample weights; Fowler calipers were used to measure width and length. The actual dimensional and weight measurements can be found in Appendix B; averages of these property values are shown in Table 2.

Testing Procedures

A Model TM or TTC2 Instron tensile tester (Figure 4) was used to measure the tensile properties of the liner samples.

Puncture resistance testing was performed on five samples every 30 days using an Instron tensile tester and a puncture specimen cage and probe which were made at Battelle. The specimen cage and probe conform to Method 9090 standards yet differ from FTMS 101:C in that the screws used to clamp the sample to the cage were replaced with quick removing clamp locks (Figure 5). The other major difference is that the puncture probe moves downward while the sample is held stationary.

Figure 3

Shape of Specimens Used for Tensile, Puncture, and Absorption/Leaching Tests

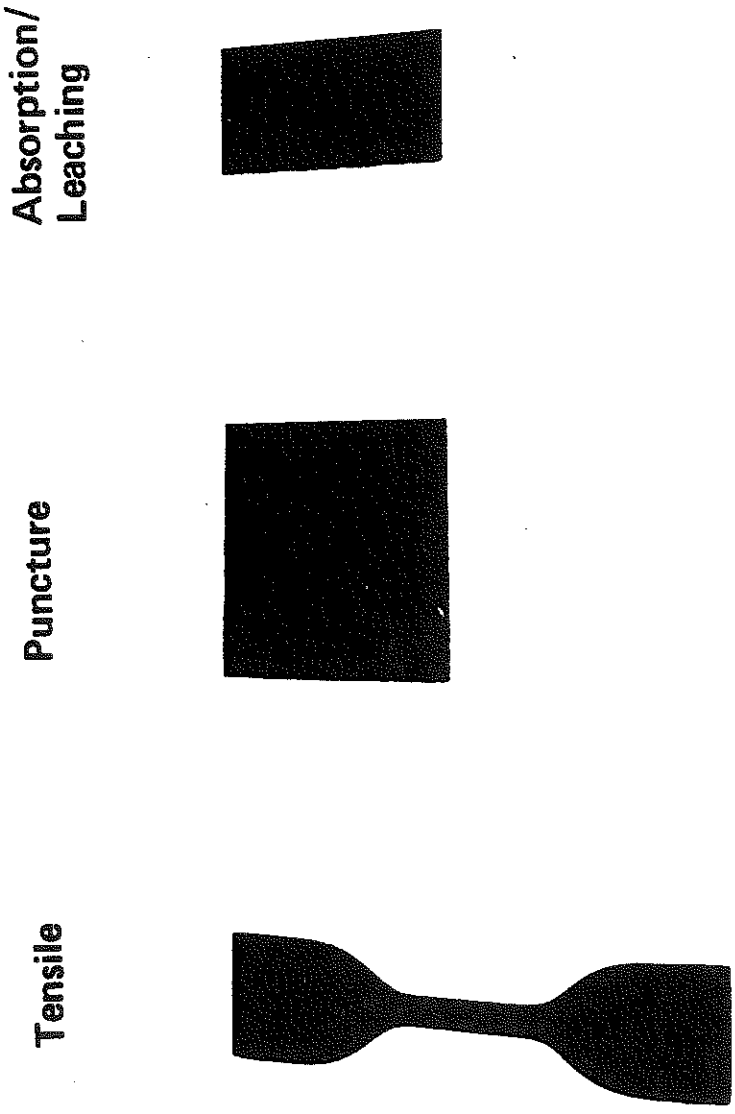


TABLE 1. MEASURED DIMENSIONS OF THE HDPE TENSILE TEST SPECIMENS

	Width, mils	Thickness, mils
$\bar{x}$(a)	245.3	65.2
s	1.1	5.1

(a) $\bar{x}$ = mean; s = standard deviation.

TABLE 2. MEASURED DIMENSIONS OF THE HDPE ABSORPTION/LEACHING TEST SPECIMENS

	Width, in.	Length, in.	Weight, g
$\bar{x}$(a)	1.008	2.002	2.021
s	0.004	0.005	0.157

(a) $\bar{x}$ = mean; s = standard deviation.

Figure 4

Tensile Sample Being Tested on a TM Instron

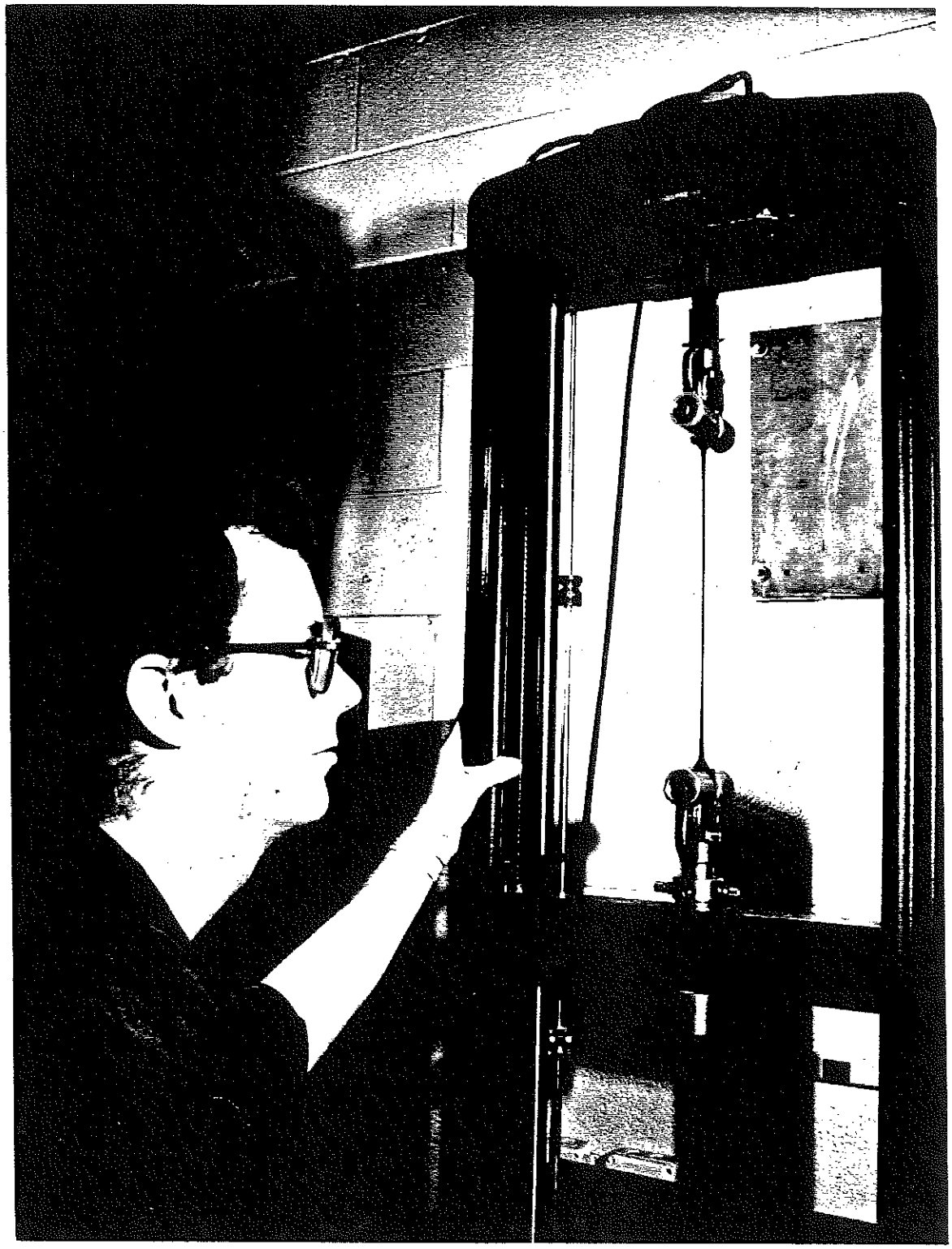
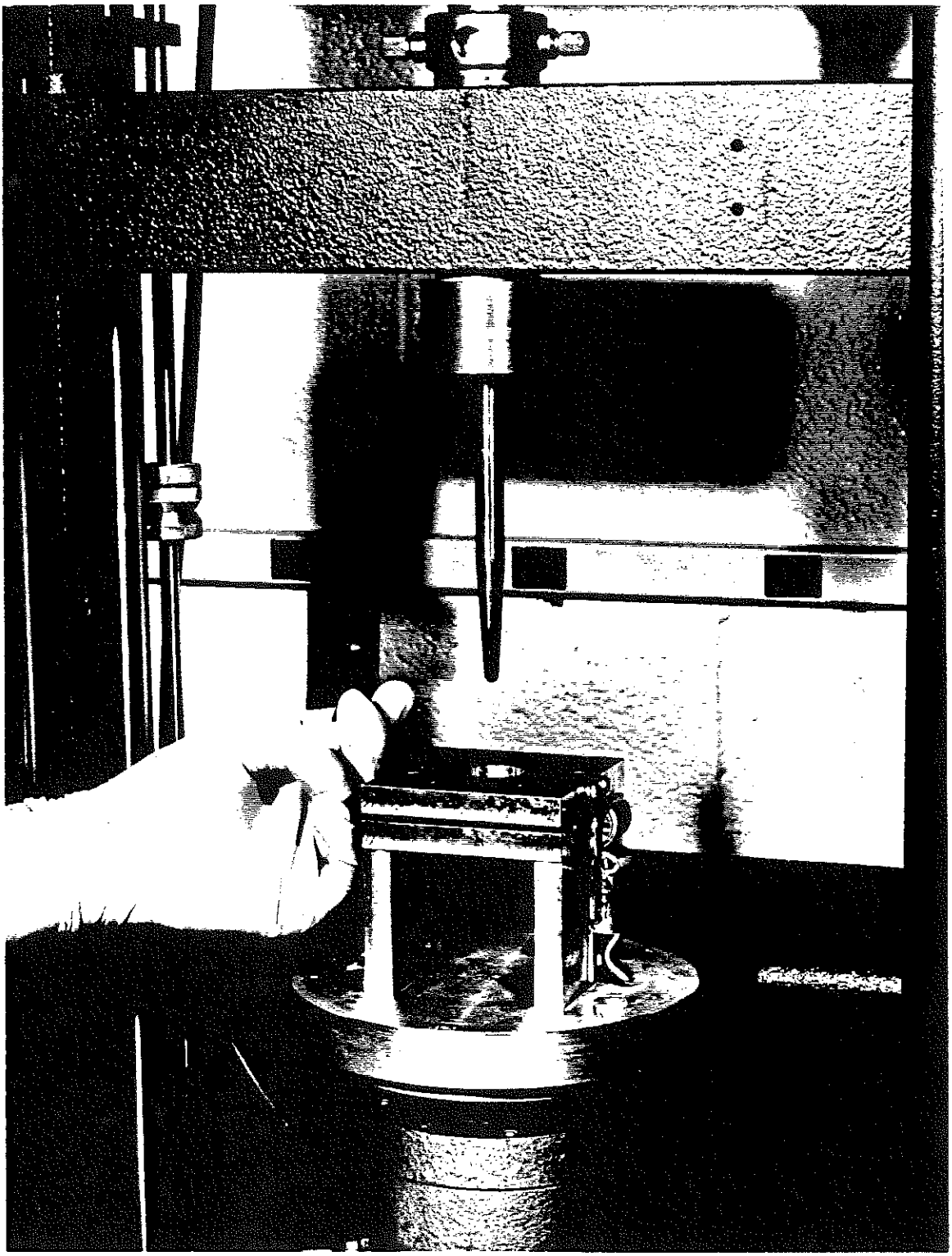


Figure 5

Specimen Cage and Probe Used to Perform Puncture Tests



Selection of Temperatures

The lower of the elevated exposure temperatures, 50 C, was selected in accordance with Method 9090. The base temperature, 13 C, was chosen because it is the expected ambient subsurface temperature at depths not affected by above-ground temperature fluctuations. As stated previously, a second elevated temperature, 80 C, was employed to provide a stress beyond that required by the current Federal rules.

Collection of Liner Samples from Exposure Chambers for Puncture, Tensile, and Absorption/Leaching Testing

The liner samples (5 or 15 of each type, for each time period, for each temperature) were removed from the exposure chambers prior to tensile, puncture, and absorption/leaching testing in accordance with Method 9090. The rack was lifted out of the leachate and set directly on the tank to allow the leachate to drip back into the tank, thus minimizing the loss of leachate at each sampling period. The absorption/leaching samples were then pulled out of the exposure chamber and put in polyethylene bags to prevent them from losing moisture. After all samples were removed from the leachate, they were taken from the bags, rinsed with deionized water, and wiped with a soft absorbant towel to remove remaining water and residual material. The absorption/leaching samples were then immediately weighted on a Mettler electronic analytical balance that reads to 0.1 milligrams.

The puncture and tensile test samples were removed from the exposure chamber and immediately placed in a one-quart jar of the appropriate Vickery leachate at room temperature for 1 hour to cool before testing. These samples were also rinsed with deionized water and wiped clean with a soft absorbing towel before being placed in polyethylene bags. These samples were tested within 24 hours after removal from the exposure chambers.

Figures 6, 7, and 8 show the sampling area and absorption/leaching and tensile samples being removed from the exposure chambers.

Figure 6

Typical Tank Setup

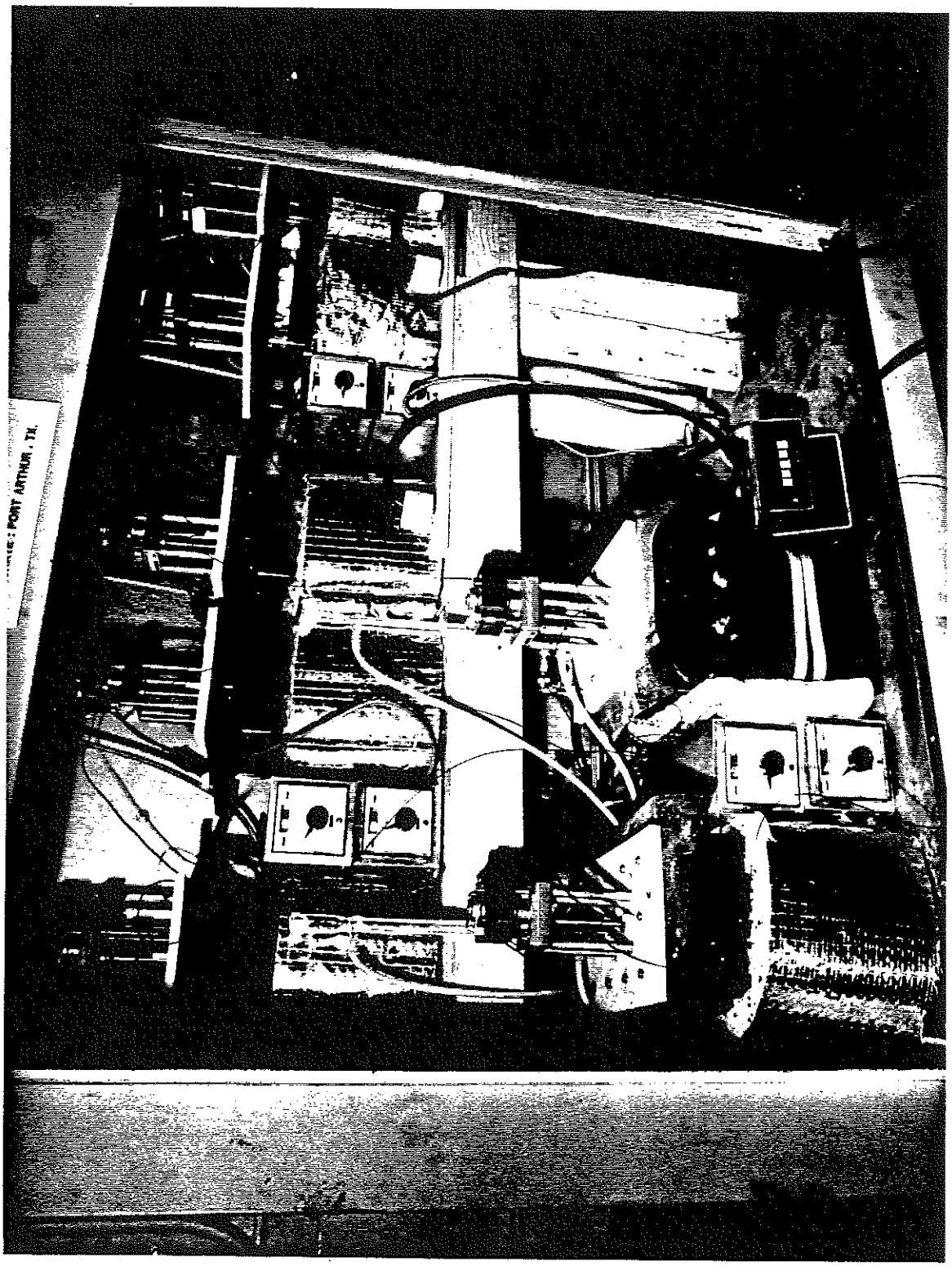


Figure 7

Absorption/Leaching Sample Being Placed in
Polyethylene Bag

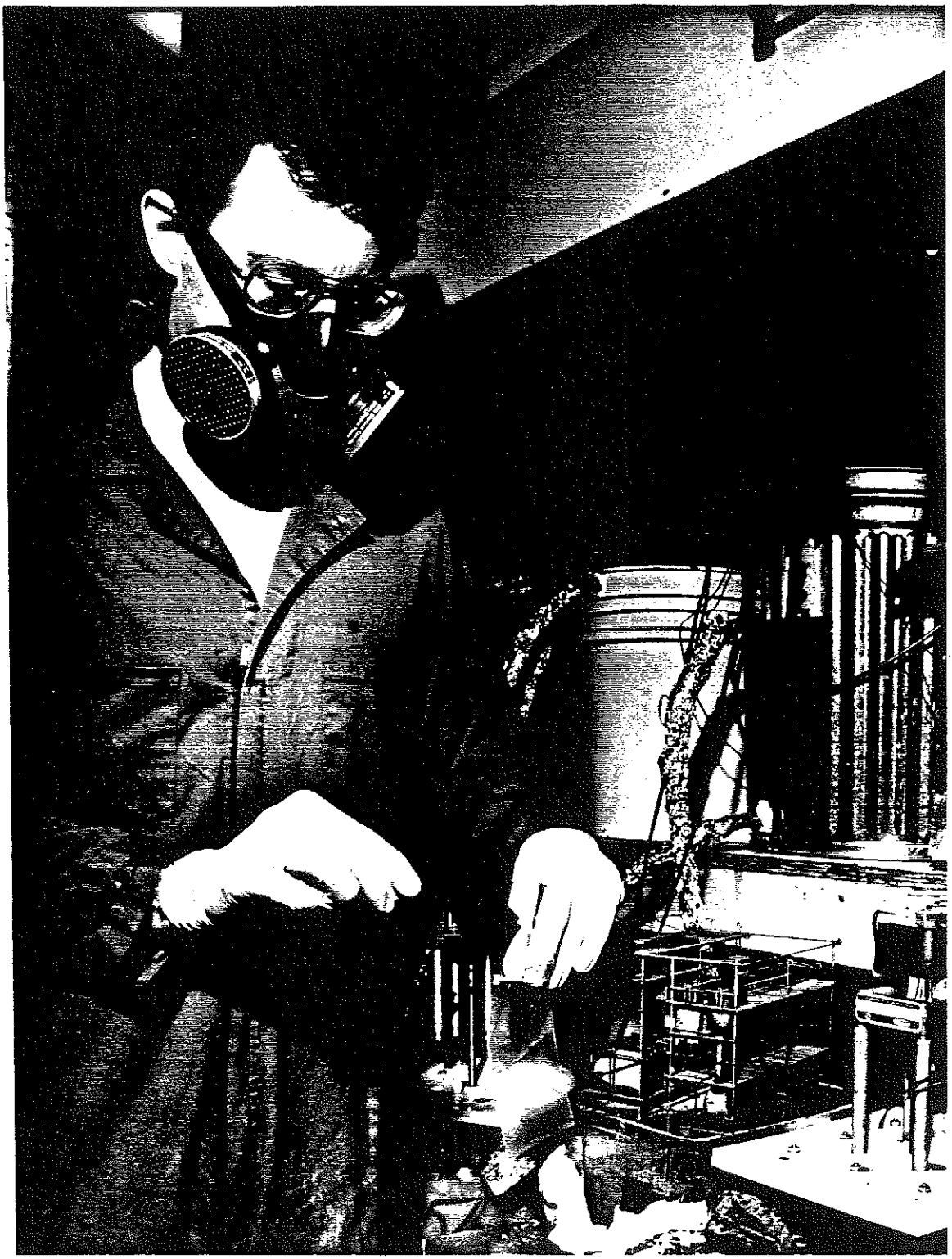
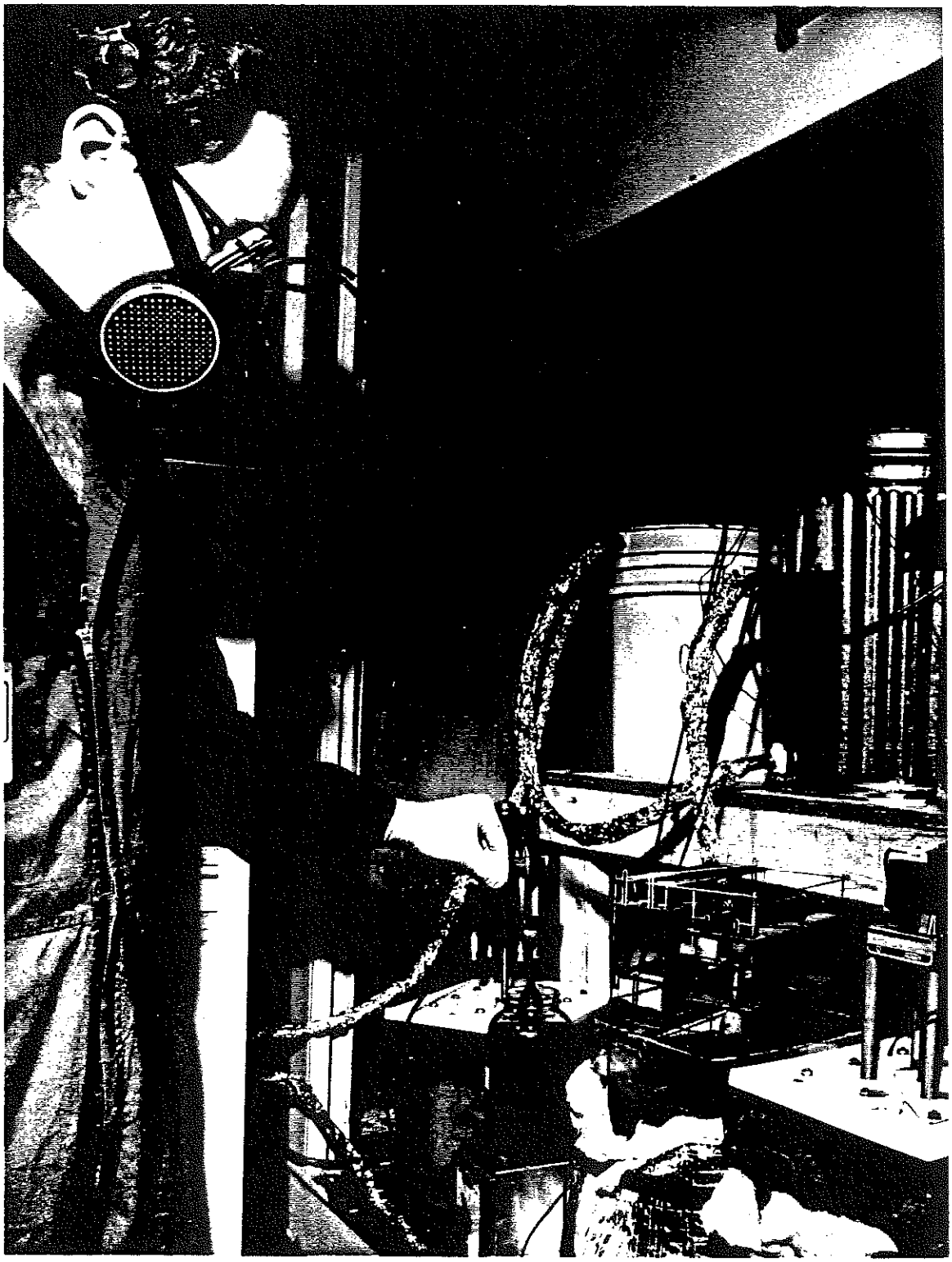


Figure 8

Tensile Sample Being Placed in
Ambient Temperature Leachate



Deviations From Method 9090

Tensile strength testing was performed only in the parallel (machine) direction. Pretest comparison of parallel and perpendicular measurement of tensile properties of the HDPE liner material showed no significant difference with respect to sample orientation (Table 3). Because there was no significant difference, tensile tests were performed only in the parallel direction.

Several researchers have investigated relationships between tear properties and tensile properties of polymers. For example, in a review of these types of investigations, Hulse[1] cites relationships between tearing energy and tensile properties such as Young's modulus and the work-to-break area (the area under the tensile stress strength curve up to rupture). Therefore, based on these relationships, changes in the tensile properties of polyethylene should reflect changes in tear strength. Because measurement of tensile properties is more straightforward than measurement of tear properties, this program concentrated on investigating the effects of leachates on the tensile properties of candidate liners.

The tensile, puncture, and absorption/leaching samples were chosen as the most efficient combination that would provide a range of physical property evaluation.

Other deviations from Method 9090 were performed to make it a more rigorous test environment. These changes included sampling five test coupons, instead of the required number of three, to give better statistical data of the testing properties, testing an additional temperature of 13 C to provide a baseline control for the statistical analyses, testing an additional temperature of 80 C to increase the stress beyond that imposed by the 50 C testing, and completely immersing the specimens of candidate barrier material in the leachate. All these changes provided additional information and more rigorous testing situation than running an unmodified Method 9090.

TABLE 3. PRETEST COMPARISON OF PARALLEL AND PERPENDICULAR TENSILE TESTING OF HDPE LINER MATERIAL

	Parallel Tensile Testing, $\bar{x}/s$[a]	Perpendicular Tensile Testing, $\bar{x}/s$[a]
Tensile Strength at Break, psi	2910/280	3170/710
Elongation at Break, %	490/80	503/120
Tensile Strength at Yield	3180/120	2890/220
Stress at 100% Elongation, psi	2400/250	2380/70
Stress at 200% Elongation, psi	2450/240	2520/120
Stress at 300% Elongation, psi	2510/260	2550/90

(a) $\bar{x}$ = average value; s = standard deviation. All values are an average of five measurements.

RESULTS

Monthly Testing Protocol

At 30, 60, and 90 days, 15 samples (5 each 1 x 2, 2 x 2, and dog bone) were pulled from the four tanks--13 C, 50 C, 80 C, and 80 C(N)*--for tests of tensile, puncture, and absorption/leaching properties. A total of 75 samples was used for the 120-day tests. The recovery and testing of the samples were performed in accordance with EPA Method 9090. Testing of the samples was completed within a day after recovery of the samples from the tanks, and the results were entered in the lab book. This information was also included in each monthly report.

All tanks were checked regularly for temperature and to be sure there was no mechanical breakdown in the system. Leachate levels also were closely observed to detect evaporation that may have taken place. If evaporation had occurred, leachate was added and the amount recorded; these data are shown in Table 4.

Precision and Accuracy of Test Methods

As previously presented, the conditions for this test program were those specified by U.S. EPA Method 9090. These conditions have been broadened considerably in an effort to permit a more refined interpretation of the results and greater confidence in the conclusions. The specified conditions of Method 9090 relate to: (1) preparation of the test specimens, (2) temperature of exposure, and (3) leachate composition. Accuracy and precision levels in the measurement of the physical condition of the HDPE liner material are discussed in the next section.

Variation in Test Specimens

As discussed previously, the dimensions of the test specimens prepared from the HDPE material are quite regular. Test specimens were die cut for the tensile specimens and shear cut for the puncture and absorption

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*The 80 C(N) designation is used hereafter to indicate the 80 degree neutralized leachate.

TABLE 4. LEACHATE VOLUMES (IN LITERS) INITIALLY, FINALLY, AND ADDED TO EXPOSURE CHAMBERS TO OFFSET EVAPORATION

Tank (Temperature)	Date	Initial Volume	Added Volume(s)	Final Volume
EC_{36} (13 C)	11/16/85	11.0		10.5
EC_{35} (50 C)	07/16/84	11.0		
	11/12/84		0.9	
	11/16/84			10.5
EC_{37} (80 C) Neutralized	11/21/84	10.0		
	12/07/84		0.6	
	12/19/84		0.4	
	01/17/85		0.7	
	02/28/85		0.5	
	03/21/85			10.0
EC_{38} (80 C)	12/07/84	10.0		
	12/17/84		0.5	
	01/07/85		0.5	
	01/17/85		0.5	
	02/28/85		0.5	
	03/13/85		0.5	
	03/28/85		0.5	
	04/07/85			10.0

specimens. Because of the close tolerances achieved with die cutting and the regularity of the HDPE film, average specimen dimensions were determined by statistical methods.

The results of the statistical analysis of 100 tensile specimens were shown in Table 1. With an average width of 245.4 mils and a standard deviation of 1.1 mils and an average thickness of 65.2 mils and a standard deviation of 5.1 mils, the expected standard deviation of the combined test method and normal variations in material properties on a tensile strength measurement would be 235 lb/square inch at an average tensile strength of 3000 lb/square inch.

Inasmuch as the thickness used for the puncture specimens was that determined from the tensile specimens, the probable error in the puncture strength measurement would be 7.0 lbs at 90 lbs.

Although the absorption specimen measurements were statistically analyzed as well, as shown in Table 2, no systematic error would be introduced in this manner because each specimen has its weight individually determined, recorded, and tracked.

Testing Temperature

The average temperatures and the variation over time under which exposure of specimens was conducted are presented in Table 5.

TABLE 5. TEMPERATURE VARIATIONS OBSERVED IN EXPOSURE TANKS, DEGREES CELSIUS

Temperature	13 C	50 C	80 C (Neutralized)	80 C
Minimum	11.7	48.9	65.6(a)	37.2(b)
Average	13.5	49.7	79.9	78.4
Maximum	15.6(b)	50.6	81.1	82.2

(a) Occurred because of mechanical failure.
(b) Measured during startup.
(c) Somewhat higher temperatures were observed for very brief periods because of the variations in temperature of laboratory tapwater used for cooling; for the 13 C tanks, the short-term maximum was 15.6 C.

Each of the preselected immersion test bath temperatures was maintained within ±2 degrees C throughout the test period except for the bath at 13 C. Differences in the average exposure tank temperature will be reflected in the rate of acceleration of time represented by the test. The 50 C test temperature is capable of accelerating 120 days of actual testing into 25 years of exposure. For example, a temperature of 49.7 C would yield an equivalent exposure time of 24.8 years, considered to be an insignificant deviation from the desired 25 year minimum.

Data Analysis and Presentation

After each testing period (30, 60, 90, and 120 days), the data from each puncture, tensile, and absorption/leaching test were reduced to the mean and standard deviation for each property. These data were included in each monthly report in table form. The total results have been consolidated into Tables 6, 7, and 8.

The data tabulated for the monthly reports were then plotted as bar graphs for each property over the time period of 0 to 120 days. These graphs are discussed in the results interpretation results section.

Results Interpretation According to EPA Method 9090

The currently applicable U.S. EPA test requirements for HDPE liners require three types of tests--tensile strength, puncture strength, and absorption/leaching determined on material specimens exposed to the expected chemical environment (Vickery leachate) for 120 days at 50 C. This test program went beyond the minimum requirements in that an additional test was conducted at 80 C to provide evidence of compatibility under more severe conditions of exposure.

Due to the inherent (and entirely normal) variability in strength testing methods and in the the liner material itself, statistical methods must be used to look for differences between leachate-exposed and control specimens. Two such tests were used to judge whether the differences were real or not. The first test, known as the Student's t-test, tests the

TABLE 6. VICKERY HDPE TEST DATA FOR TENSILE PROPERTIES

Sample ID	Time days	Tensile Break Strength psi mean	Tensile Break Strength psi std.dev.	Tensile Yield Strength psi mean	Tensile Yield Strength psi std.dev.	Tensile Elongation at Break percent mean	Tensile Elongation at Break percent std.dev.
VICKERY SUMMARY DATA, 13C							
V-36	30	2480	35.8	3410	67.2	460	52.9
V-36	61	2450	95.9	3450	108	444	67.9
V-36	91	2550	220	3540	68.4	315	195
V-36	121	2600	260	3410	87.2	464	86.4
VICKERY SUMMARY DATA, 50C							
V-35	30	2370	95.5	3390	89.8	399	104
V-35	61	2530	132	3550	108	474	66
V-35	91	2570	109	3600	52.6	347	129
V-35	121	2480	90.6	3540	106	397	97.9
VICKERY SUMMARY DATA, 80C (UNNEUTRALIZED)							
V-38	31	2690	84.4	3740	95	284	149
V-38	60	2360	98.6	3550	121	244	143
V-38	90	2710	166	3850	66.3	332	128
V-38	119	2610	113	3810	124	257	121
VICKERY SUMMARY DATA, 80C (NEUTRALIZED)							
V-37	30	2450	104	3550	76.6	311	122
V-37	62	2510	213	3700	58.6	274	140
V-37	90	2360	77.1	3640	94.1	207	100
V-37	120	2410	99.5	3650	102	227	113
CONTROL DATA							
C-30		2480	111	3500	44.3	435	84.9
C-60		2480	111	3500	44.3	435	84.9
C-90		2640	107	3640	144	411	101
C-120		2600	102	3670	80.6	395	111

TABLE 7. VICKERY HDPE TEST DATA FOR PUNCTURE PROPERTIES

Sample ID	Time days	Puncture Break Strength pounds mean	Puncture Break Strength pounds std.dev.	Puncture Yield Strength pounds mean	Puncture Yield Strength pounds std.dev.	Puncture Elongation at Break percent mean	Puncture Elongation at Break percent std.dev.
VICKERY SUMMARY DATA, 13C							
V-36	30	81	2.05	90	1.73	1070	73.5
V-36	61	84	0.837	91	1.14	1190	49.3
V-36	91	84	4.85	91	3.96	1160	75.3
V-36	121	87	2.68	92	2.17	1150	79.5
VICKERY SUMMARY DATA, 50C							
V-35	30	83	0.894	94	2	1070	40.2
V-35	61	80	1.92	87	3.74	1100	49.3
V-35	91	86	2.79	93	2.45	1100	49.3
V-35	121	83	3.46	93	2.77	1040	55.7
VICKERY SUMMARY DATA, 80C (UNNEUTRALIZED)							
V-38	31	88	2.17	100	3.29	1050	43.8
V-38	60	79	3.36	96	2.68	917	59
V-38	90	86	1.82	103	1.67	983	37.1
V-38	119	86	2.28	103	3.36	1010	52
VICKERY SUMMARY DATA, 80C (NEUTRALIZED)							
V-37	30	85	3.37	93	3.85	1080	60.2
V-37	62	84	3.13	97	3.39	1000	0
V-37	90	86	4.36	97	2.55	983	37.1
V-37	120	87	2.79	99	3.81	1010	41.8
CONTROL DATA							
C-30		75	2.98	88.3	3.27	1010	73.8
C-60		75	2.98	88.3	3.27	1010	73.8
C-90		88.3	2.75	95.2	1.32	1160	56.9
C-120		83.3	3.92	96.7	2.24	990	137

TABLE 8. VICKERY HDPE TEST DATA FOR SORPTION PROPERTIES

Sample ID	Time days	Sorption Weight Change percent mean	std.dev.	Sorption Weight Change mg. mean	std.dev.
VICKERY SUMMARY DATA, 13C					
V-36	30	0.981	0.84	24	14
V-36	61	0.2	0.21	3	5
V-36	91	1.1	0.593	17	26
V-36	121	1.31	0.604	15	23
VICKERY SUMMARY DATA, 50C					
V-35	30	0.543	0.475	30	14
V-35	61	1.78	0.236	33	5
V-35	91	2.04	1.13	38	21
V-35	121	1.84	1.28	30	29
VICKERY SUMMARY DATA, 80C (UNNEUTRALIZED)					
V-38	31	0.966	0.164	18	0.5
V-38	60	0.894	0.0209	17	0.2
V-38	90	1.04	0.0401	20	1
V-38	119	1.1	0.0151	21	0.6
VICKERY SUMMARY DATA, 80C (NEUTRALIZED)					
V-37	30	2.5	0.503	47	9
V-37	62	3.12	0.16	58	3
V-37	90	3.03	0.214	57	5
V-37	120	3.04	0.591	58	11

hypothesis of whether the means (arithmetic averages) of two samples (in this case leachate-exposed and control specimens) are different at some level of probability. The typical value used in such tests is the 95 percent level, indicating that 19 times out of 20 the test will correctly indicate the difference. Particular attention was paid to the 120-day results in comparison with those on the earlier test dates because it is the final condition of the material that is of greatest concern in determining long-term compatibility.

As a second test, the trend of a given property measurement such as tensile strength, over time, i.e., 0-120 days, is of interest. Whether the property measurement is significantly decreasing over time (indicating a deterioration in the property), is increasing over time (indicating an improvement), or is not changing significantly over time is determined. The statistical test consists of identifying the best straight line that can be fit to the data and determining whether the slope of that line is significantly greater or less than zero. As before, the definition of significance allows for a correct judgment 19 times in 20.

Finally, the engineering properties themselves are examined to determine whether the values are beyond limits of tolerance for the materials. This type of evaluation is especially important for the sorption tests because small weight gains or losses are inconsequential.

Statistical Analysis Results

The results on test specimens exposed to EP leachate were compared with control samples held at room temperature in distilled water. The procedure was modified after the 30-day test to run control samples with each set of coupons rather than have a single set apply to all treatment coupons. The Student's t-test was applied to the specimens withdrawn each 30 days to determine any statistically significant differences between test specimens and control specimens.

$$t = \frac{\bar{X}_1 - \bar{X}_0}{S\left(\frac{1}{n_1} + \frac{1}{n_0}\right)^{1/2}}$$

$$s^2 = (f_1 s_1^2 + f_0 s_0^2)/(f_1 + f_0)$$

where:

$\bar{X}_1$ = average property value for test specimens

$\bar{X}_0$ = average property value for control specimens

n_1 = number of test specimens used for the measurement, (n_1 = 5 for 30, 60, 90 day day tests and 15 for 120 day tests).

Tensile Strength

Data were graphed for the three tensile properties in Figure 9, 10, and 11. Mean values for both the test specimens and the control specimens were plotted for each of the indicated time periods. The standard deviation associated with each mean property value was indicated by the following symbol, I.

The overlap of the deviations as well as the closeness of the test specimens means to the control specimen means suggested no degradation. Table 9 summarizes the significant t-test and regression line slopes. For tensile yield strength, 8 of the 16 possible time-temperature combinations were significant; yet, positive slopes corresponding with each regression line indicated enhancement rather than degradation of the tensile yield strength. Only 4 out of 16 possible time-temperature combinations for tensile break strength had a significant t-test. With the exception of the 80 C(N) data, all the regression lines had positive slopes again indicating enhancement of the tensile break strength. Tensile elongation had 7 out of 16 significant t-test values. The positive slopes of the regression lines (with the exception of the 80 C(N) data) indicated improvement in tensile elongation at break. The negative slope associated with the 80 C(N) elongation at break data simply indicated a reduction in the plasticity of the liner material. The reduction in elongation over time was not significant and, combined with the lack of a strength loss, the elongation changes are deemed to be of minor consequence.

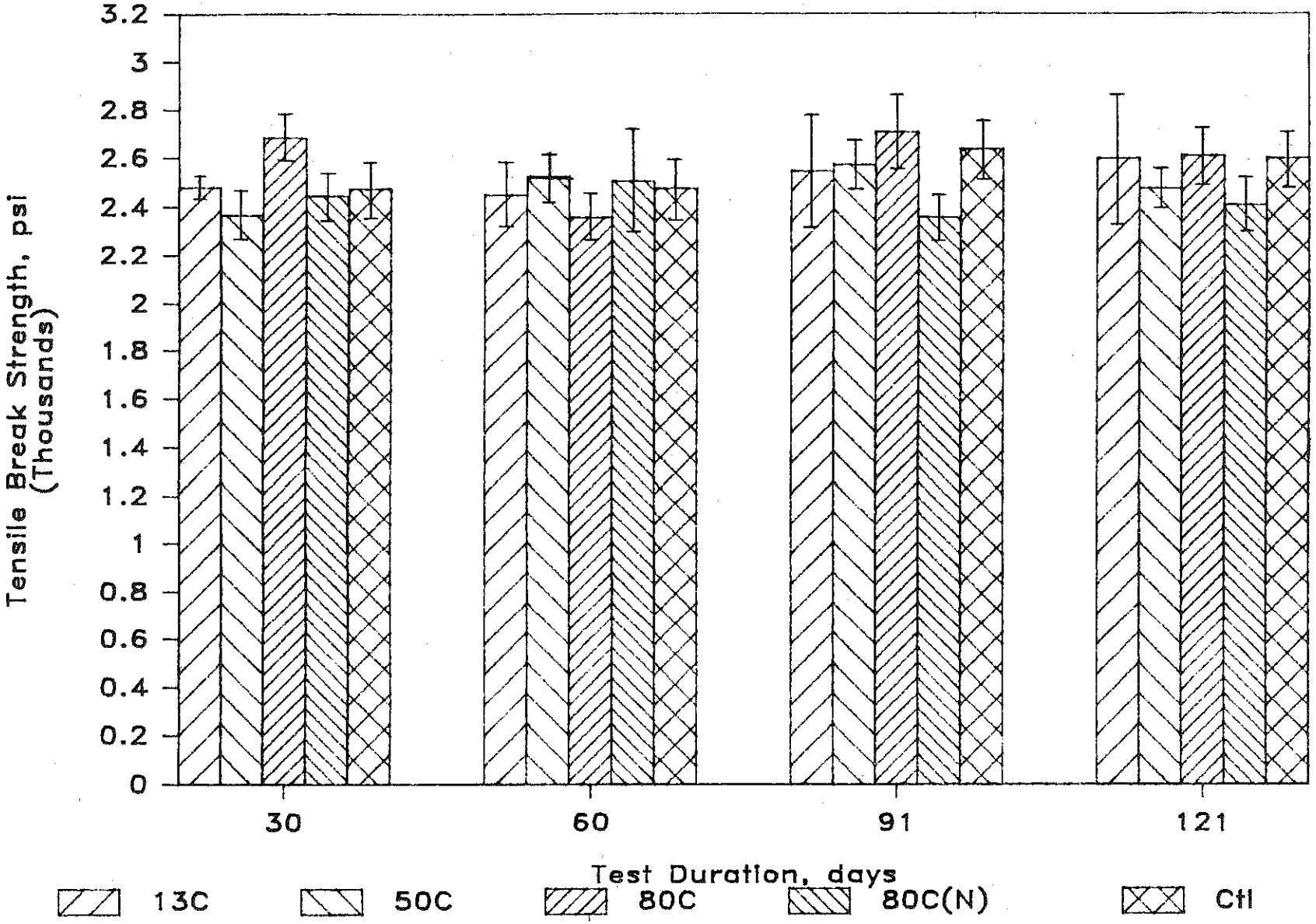

FIGURE 9. TENSILE BREAK STRENGTH

Standard deviations are indicated by : I

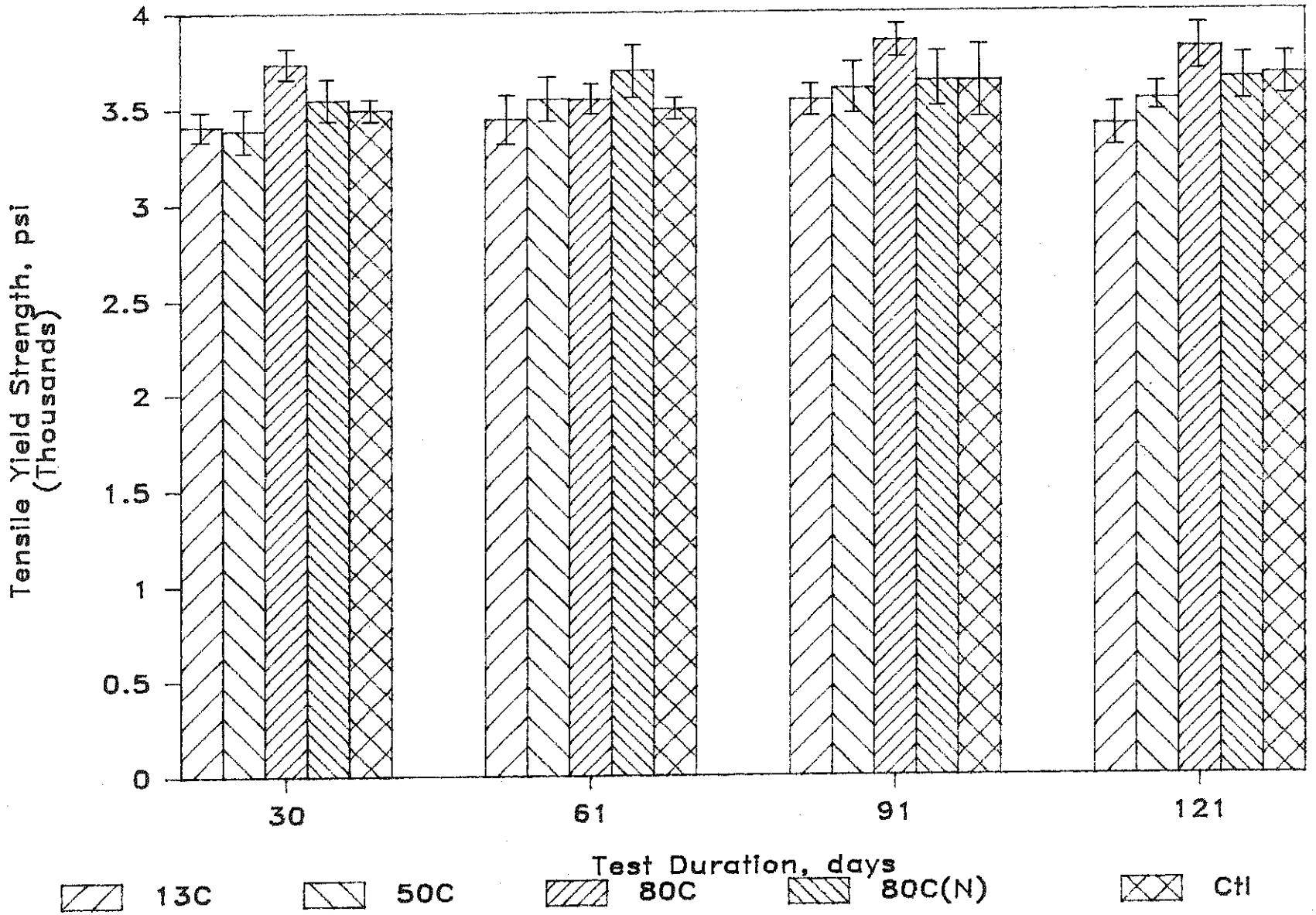

FIGURE 10. TENSILE YIELD STRENGTH

Standard deviations are indicated by: I.

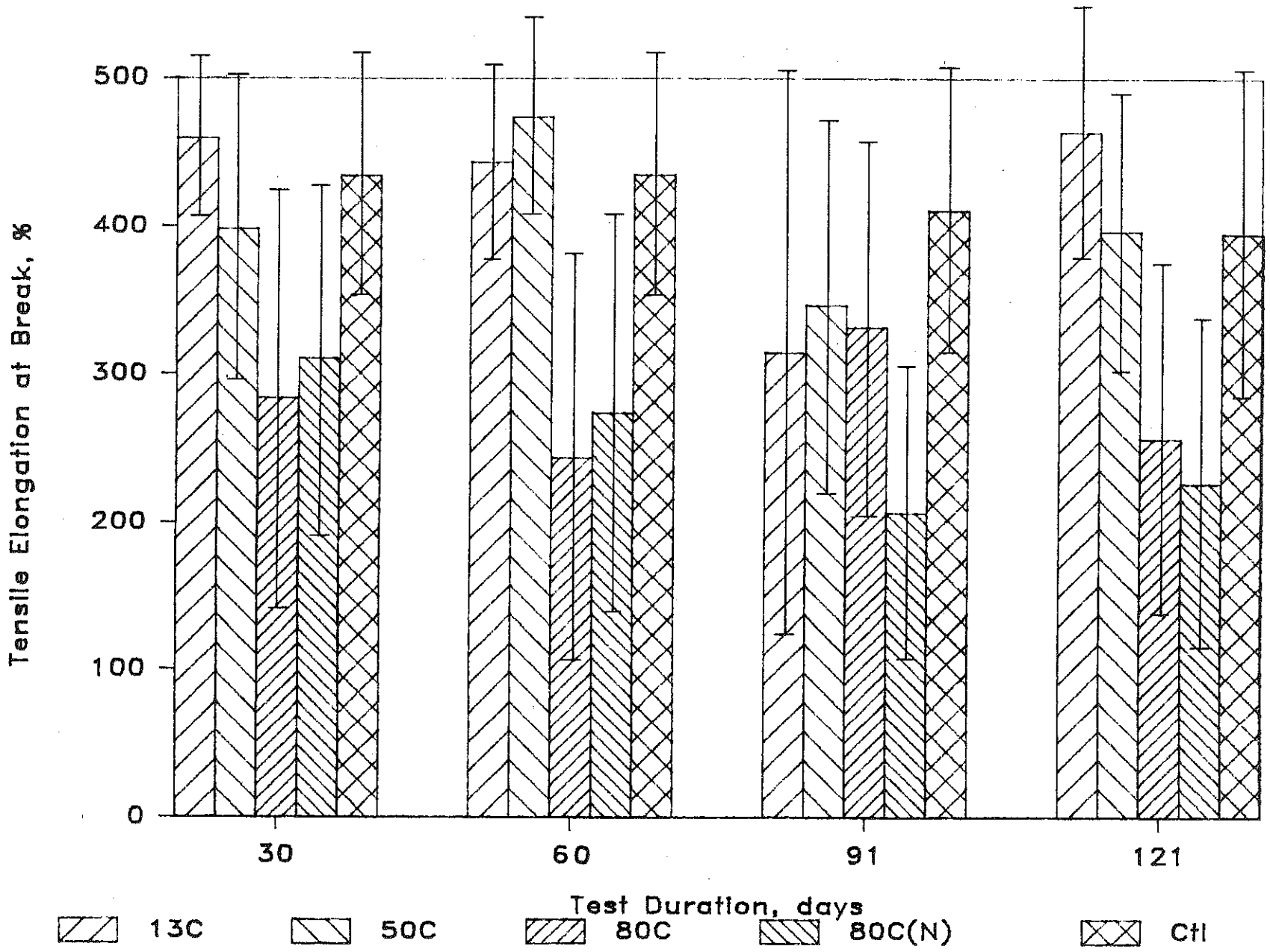

FIGURE 11. TENSILE ELONGATION AT BREAK

Standard deviations are indicated by: I

TABLE 9. T-TEST RESULTS AND REGRESSION LINE SLOPES FOR TENSILE PROPERTIES SIGNIFICANT AT THE 5 PERCENT LEVEL (95 PERCENT CONFIDENCE INTERVAL)

	Tensile Yield Strength, (psi)	Tensile Break Strength, (psi)	Tensile Elongation at Break, (percent)
30 days:			
13 C	X		
50 C	X		
80 C	X	X	X
80 C(N)			X
60 days:			
13 C			
50 C			
80 C			X
80 C(N)	X		X
90 days:			
13 C			
50 C			
80 C	X		
80 C(N)		X	X
120 days:			
13 C	X		
50 C	X	X	
80 C	X		X
80 C(N)		X	X
Regression Line Slope			
13 C			
50 C			
80 C	X(I)[a]		
80 C(N)			

(a) I = increasing with time.

Puncture Strength

Figures 12, 13, and 14 depict the puncture properties data. Once again, mean values for both test and control specimens were plotted against time with standard deviations indicated by the following symbol, I.

In general, the closeness of the test means to the control means suggested no degradation. A summary of the t-test data and regression line slopes appears in Table 10. For puncture yield strength, 8 of the possible 16 time-temperature combination had significant t-test; however, the positive slopes of the regression lines indicated an enhancement of the puncture yield strength. Similarly, the puncture break strength had a number of significant t-test results; yet, all the regression lines had positive slopes indicating an improvement in the puncture break strength. Puncture elongation at break, on the other hand, had only 6 out of 16 significant t-test results; but the majority of the regression lines had a negative slope indicating a reduction in the plasticity of the material. The reduction in elongation over time was not significant. In combination with the lack of a loss in strength properties, the lower elongation values are felt to be of minor consequence for compatibility.

Sorption

Graphs for sorption weight change were plotted as both mass (in milligrams) and percentage (Figures 15 and 16). Sorption weight changes on the order of 10 percent are required to produce significant deterioration of polymer properties. Inasmuch as the observed changes did not exceed 3.5 percent and were typically in the 1.0-1.8 percent range, the change in liner sorption properties over time was deemed insignificant. When comparing the neutralized 80 C data with the unneutralized 80 C data, a substantial increase was observed in the sorption associated with the neutralized leachate suggesting a possible base catalyzed sorption reaction.

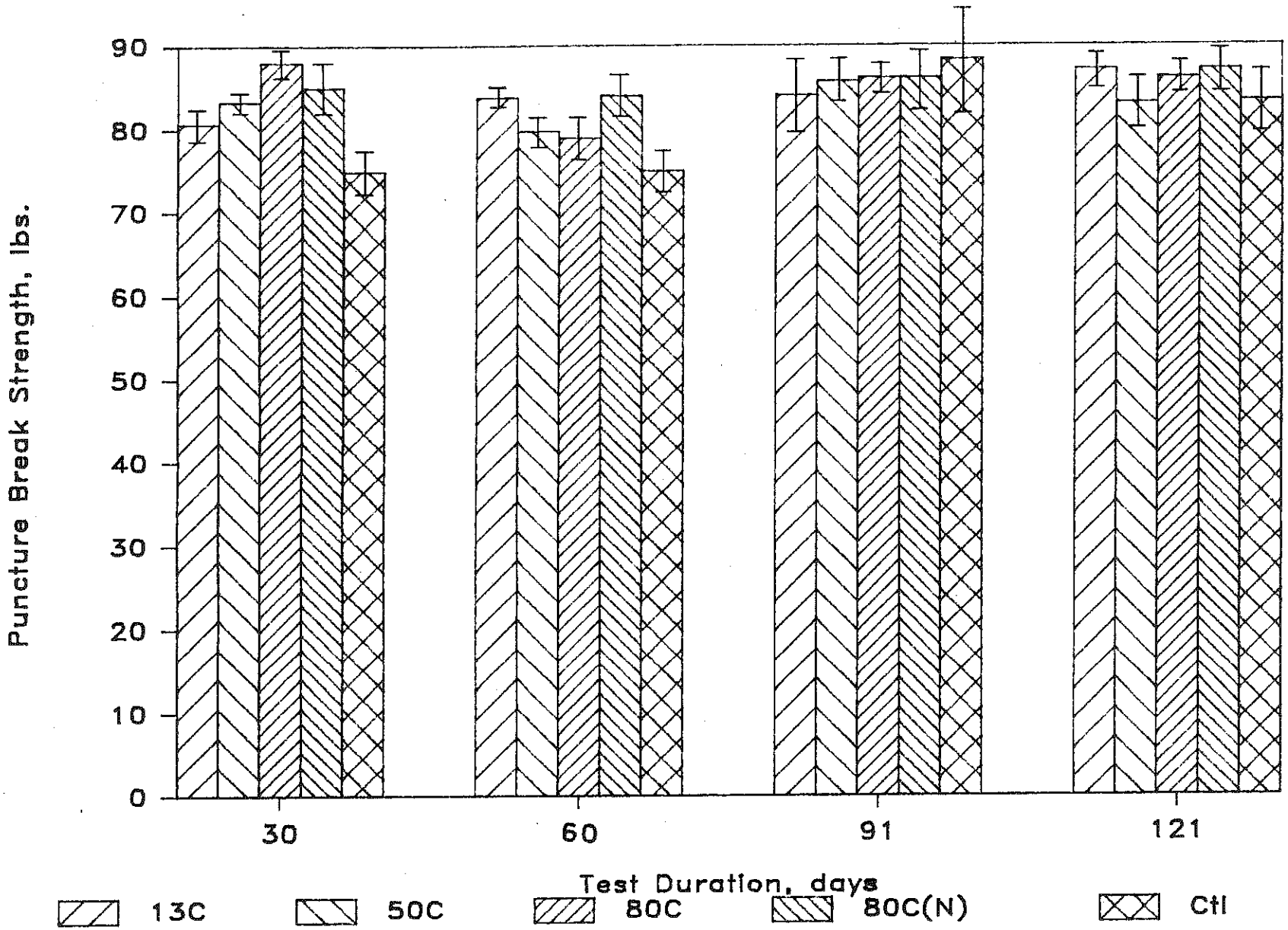

FIGURE 12. PUNCTURE BREAK STRENGTH

Standard deviations are indicated by: I

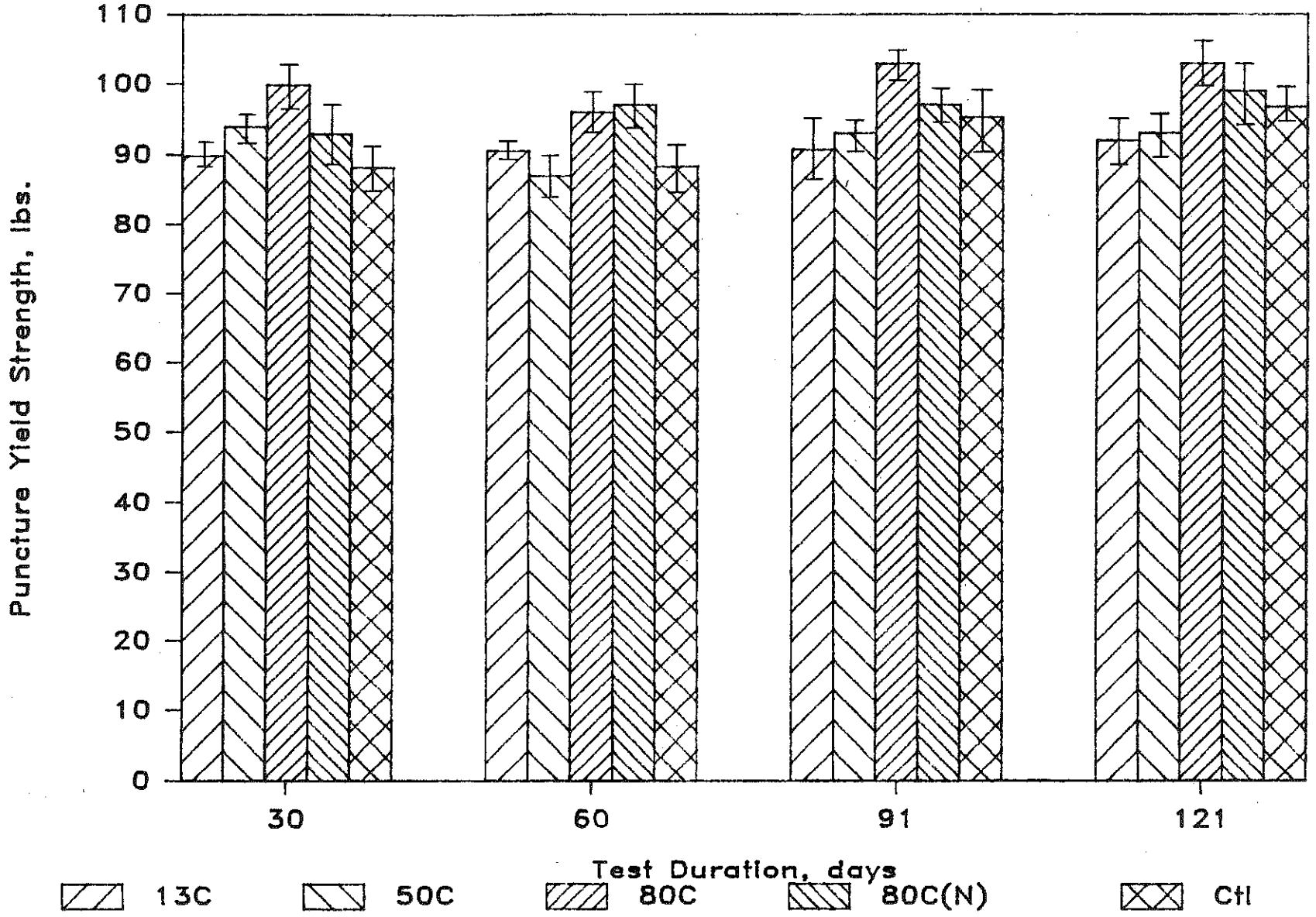

FIGURE 13. PUNCTURE YIELD STRENGTH

Standard deviations are indicated by: I

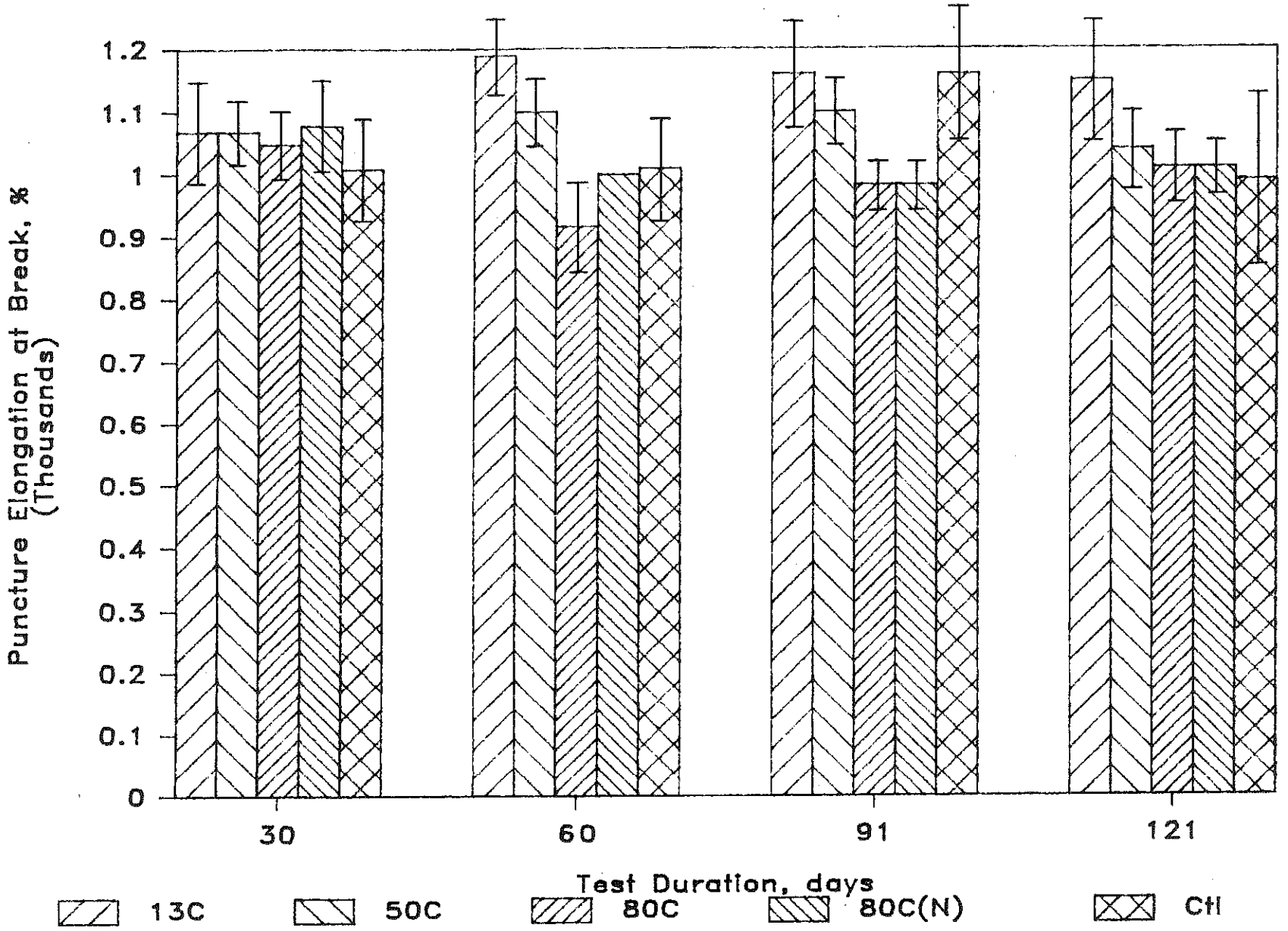

FIGURE 14. PUNCTURE ELONGATION AT BREAK

Standard deviations are indicated by: I

TABLE 10. T-TEST RESULTS AND REGRESSION LINE SLOPES FOR PUNCTURE PROPERTIES SIGNIFICANT AT THE 5 PERCENT LEVEL (95 PERCENT CONFIDENCE INTERVAL)

	Puncture Yield Strength, (pounds)	Puncture Break Strength, (pounds)	Puncture Elongation at Break, (percent)
30 days:			
13 C		X	
50 C	X	X	
80 C	X	X	
80 C(N)	X	X	
60 days:			
13 C		X	X
50 C		X	X
80 C	X	X	X
80 C(N)	X	X	
90 days:			
13 C			
50 C			
80 C	X		X
80 C(N)			X
120 days:			
13 C	X	X	X
50 C			
80 C	X		
80 C(N)		X	
Regression Line Slope			
13 C		X(I)[a]	
50 C			
80 C			
80 C(N)			

(a) I = Increasing with time.

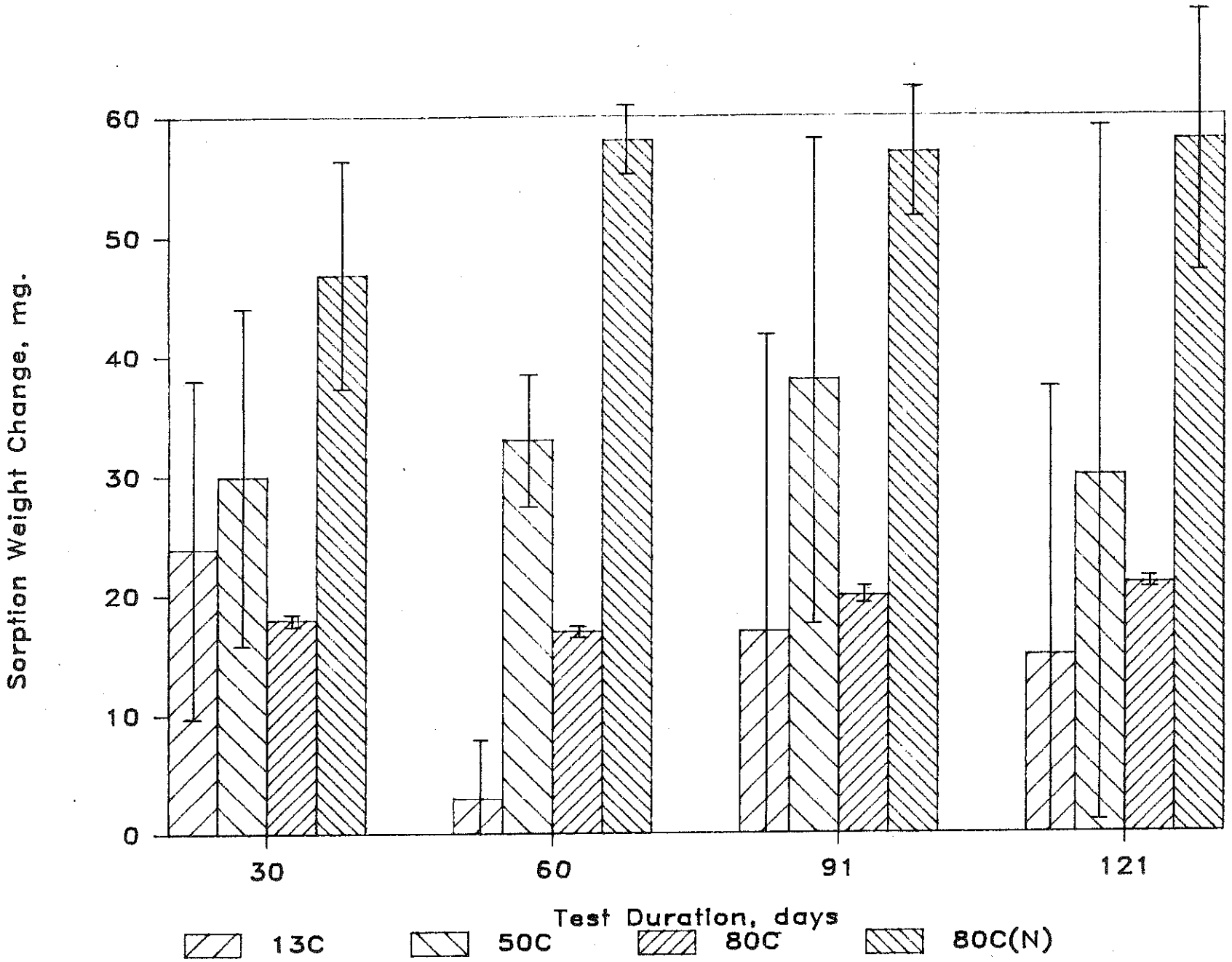

FIGURE 15. SORPTION WEIGHT CHANGE

Standard deviations are indicated by: I

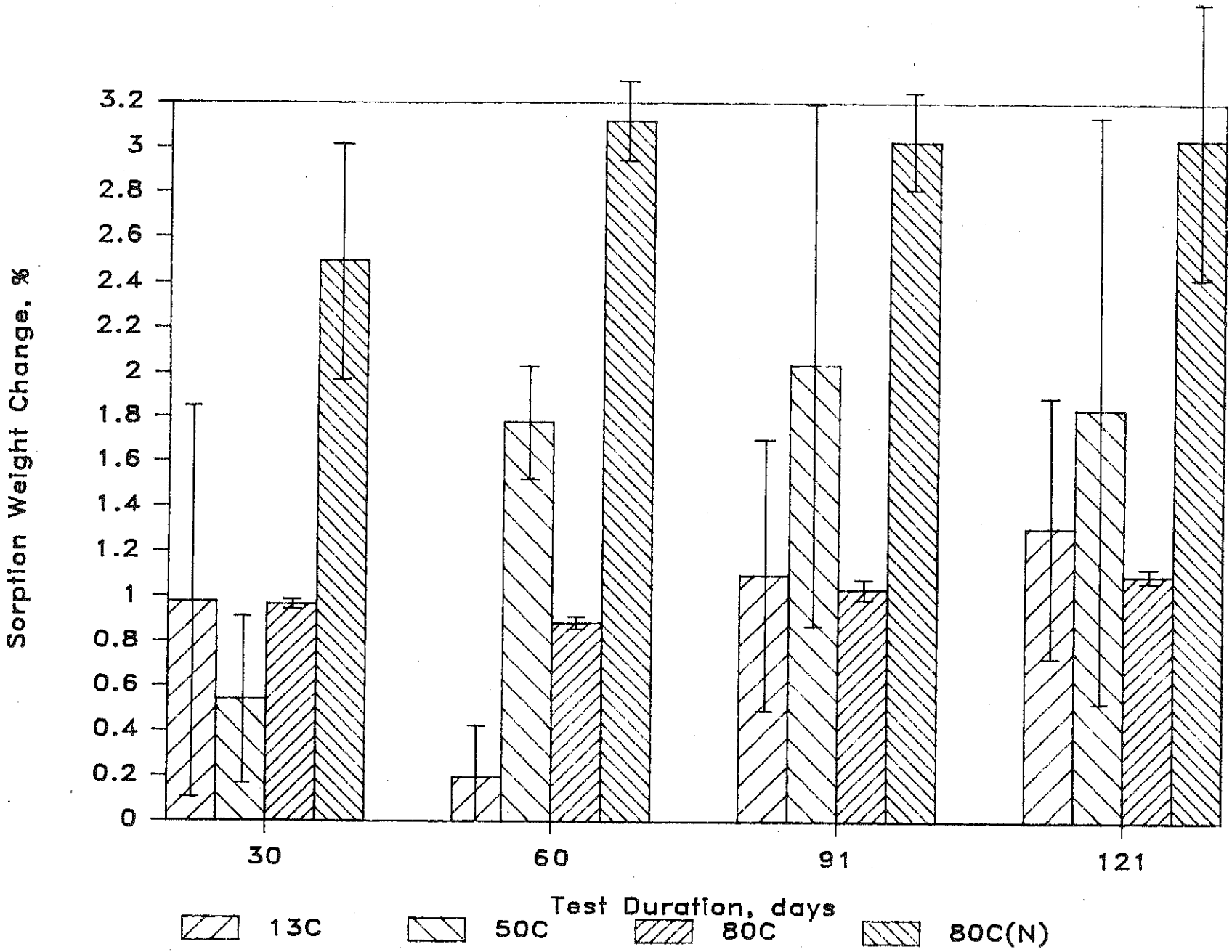

FIGURE 16. PERCENT SORPTION WEIGHT CHANGE

Star ·d deviations are indicated by: I

CONCLUSIONS

Extensive tests were performed on HDPE material exposed to leachate generated from sludge obtained at Chemical Waste Management's Vickery, Ohio site. The test specimens were carefully maintained at 13, 50 and 80 C to provide baseline and accelerated testing of the liner material. The 50 C tests, and especially the 80 C tests, which represent a more severe exposure than that required by current EPA procedures, were used to judge whether deterioration had occurred.

The tensile tests (tensile break strength, tensile yield strength and elongation) showed that the material loses some plasticity at the highest temperature but exhibits no loss in strength. In fact, there is a general improvement in strength at the lower temperatures. It is therefore concluded that no significant changes in tensile properties occurred.

The puncture tests (puncture break strength, puncture yield strength and elongation) showed essentially the same trends with time and temperature. It is concluded that no significant changes in puncture properties occurred.

Finally, the sorption weight changes were well below 10 percent; so, it is concluded that no significant sorption occurred. (Negative weight changes were not observed.)

The U.S. Environmental Protection Agency has provided guidance in the interpretation of the above stated conclusions with regard to long-term compatibility. This guidance derives from the expectation that the rate of attack of leachate components on the liner is a chemical reaction-rate controlled process (49FR38786, October 1, 1984):

"The liner compatibility test (Method 9090) employs a short exposure of the liner to the chemical environment at two temperatures, room temperature (assumed room temperature) 10 C and 50 C, to simulate effects of a waste on a liner, including long-term effects. Since actual field testing would require 25 years or more, EPA decided that the test could be shortened to a 120 day maximum by increasing the temperature of some of the testing to 50 C."

The temperature of 50 C and the test period length were chosen using the Arrhenius equation:

$$r = Ae^{-E_a/RT} \quad ,$$

where r is the reaction rate at an absolute temperature, T, for a reaction with an activation energy, E_a, (estimated to be 20 kcal/mole). (A is a proportionality factor which divides out when the ratio of the rates is computed.)

Based on the ratio of the rates at the two specified temperatures, the reaction rate acceleration factor of more than 75 allows 25 years of room temperature exposure to be compressed into 120 days.

No significant degradation in liner properties was observed during the test period at 50 C. It is concluded that leachate of a type similar to that which could be generated is compatible with HDPE liner material for a minimum of 25 years. The additional test at 80 C confirms this conclusion and indicates that the liner should last well in excess of 25 years.

REFERENCES

(1) Physics of Plastics, edited by P.D. Ritchie, Iliffe Books, Ltd., London (1965), "Other Mechanical Properties of High Polymers" (G. Hulse), pp. 152-163.

(2) Thomas, Ralph E., "Accelerated Life Testing Without Failures", submitted for publication, August, 1984.

(3) Mann, Nancy R., Schafer, Ray E., and Singpurwalla, Nozer D., Methods for Statistical Analysis of Reliability and Life Data, John Wiley & Sons, New York (1974).

APPENDIX A

SUMMARY OF U.S. EPA EXTRACTION PROCEDURE AND METHOD 9090

APPENDIX A

EXTRACTION PROCEDURE (EP)[a]

1. A representative sample of the waste to be tested (minimum size, 100 grams) should be obtained using the methods specified in Appendix I or any other methods capable of yielding a representative sample within the meaning of Part 260. (For detailed guidance on conducting the various aspects of the EP see "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods," SW-846, U.S. Environmental Protection Agency Office of Solid Waste, Washington, D.C. 20460.)

2. The sample should be separated into its component liquid and solid phases using the method described in "Separation Procedure" below. If the solid residue[b] obtained using this method totals less than 0.5% of the original weight of the waste, the residue can be discarded and the operator should treat the liquid phase as the extract and proceed immediately to Step 8.

3. The solid material obtained from the Separation Procedure should be evaluated for its particle size. If the solid material has a surface area per gram of material equal to, or greater than, 3.1 cm^2 or passes through a 9.5 mm (0.375 inch) standard sieve, the operator should proceed to Step 4. If the surface area is smaller or the particle size larger than specified above, the solid material should be prepared for extraction by crushing, cutting, or grinding the material so that it passes through a 9.5 mm (0.375 inch) sieve or, of the material is in a single piece, by subjecting the material to the "Structural Integrity Procedure" described below.

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a. United States Environmental Protection Agency, 1982, Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods. Second ed., U.S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C. SW-846.

b. The percent solids is determined by drying the filter pad at 80°C until it reaches constant weight and then calculating the percent solids using the following equation: (weight of pad + solid) - (tare weight of pad) x 100 = % solids initial weight of sample.

4. The solid material obtained in Step 3 should be weighed and placed in an extractor with 16 times its weight of deionized water. Do not allow the material to dry prior to weighing. For purposes of this test, an acceptable extractor is one which will impart sufficient agitation to the mixture to not only prevent stratification of the sample and extraction fluid but also ensure that all sample surfaces are continuously brought into contact with well mixed extraction fluid.

5. After the solid material and deionized water are placed in the extractor, the operator should begin agitation and measure the pH of the solution in the extractor. If the pH is greater than 5.0, the pH of the solution should be decreased to 5.0 $\pm$ 0.2 by adding 0.5N acetic acid. If the pH is equal to or less than 5.0, no acetic acid should be added. The pH of the solution should be monitored, as described below, during the course of the extraction and if the pH rises above 5.2, 0.5N acetic acid should be added to bring the pH down to 5.0 $\pm$ 0.2. However, in no event shall the aggregate amount of acid added to the solution exceed 4 ml of acid per gram of solid. The mixture should be agitated for 24 hours and maintained at 20 to 40 C (68 to 104 F) during this time. It is recommended that the operator monitor and adjust the pH during the course of the extraction with a device such as the Type 45-A pH Controller manufactured by Chemtrix, Inc., Hillsboro, Oregon 97123 or its equivalent, in conjunction with a metering pump and reservoir of 0.5N acetic acid. If such a system is not available, the following manual procedure shall be employed:

(a) A pH meter should be calibrated in accordance with the manufacturer's specifications.

(b) The pH of the solution should be checked and, if necessary, 0.5N acetic acid should be manually added to the extractor until the pH reaches 5.0 $\pm$ 0.2. The pH of the solution should be adjusted at 15-, 30-, and 60-minute intervals, moving to the next longer interval if the pH does not have to be adjusted more than 0.5N pH units.

(c) The adjustment procedure should be continued for at least 6 hours.

(d) If, at the end of the 24-hour extraction period, the pH of the solution is not below 5.2 and the maximum amount of acid (4 ml per gram of solids) has not been added, the pH should be adjusted to 5.0 + 0.2 and the extraction continued for an additional four hours, during which the pH should be adjusted at 1-hour intervals.

6. At the end of the 24-hour extraction period, deionized water should be added to the extractor in an amount determined by the following equation:

$V = (20)(W)-16(W)-A$

V = ml deionized water to be added

W = weight in grams of solid charged to extractor

A = ml of 0.5N acetic acid added during extraction.

7. The material in the extractor should be separated into its component liquid and solid phases as described under "Separation Procedure."

8. The liquids resulting from Steps 2 and 7 should be combined. This combined liquid (or the waste itself if it has less than 1/2 percent solids, as noted in Step 2) is the extract and should be analyzed for the presence of any of the contaminants specified in Table 1 of 261.24 using the Analytical Procedures designated below.

SUMMARY OF U.S. EPA METHOD 9090

Method 9090 is an experimental procedure to determine long-term compatibility of liner material exposed to leachate for a period of 120 days at one elevated temperature. To measure this compatibility, physical properties of the liner material are tested before and after the liner has been exposed to the leachate. The results should provide an estimate of the properties of the liner material at the time of site closure. The method is described below.

Use an exposure tank large enough to contain liner specimen samples and to support the samples so they do not touch the tank's bottom or sides. Maintain the tank temperature at 50 ± 2 C. Equip the tank with the means to prevent evaporation of the solution (e.g., cover equipped with a reflux condenser).

To obtain a representative sample, conduct sample collection, sample preservation, and leachate handling in accordance with Code of Federal Regulations 254.221(a) and (c), 264.228(a), 264.251(a), 264.252, and 264.253, 264.301(a) and 264.310(a).

Perform the following tests on unexposed samples of the HDPE.

1. Tear resistance, machine and transverse directions, five specimens each direction for nonreinforced liner materials only
2. Puncture resistance, five specimens, FTMS 101B, Method 2065
3. Tensile properties, machine and transverse directions, five tensile specimens each direction
4. Hardness, Duro A (Duro D if Duro A reading is greater than 80), ASTM D2240
5. Elongation at break, to be performed only on membrane material that does not have a fabric or other nonelastomeric support on its reverse (away-from-waste) face.

Cut the liner material to fit the sample holders and cut enough samples to have at least three samples for each waste and each exposure period. Measure these samples for the following characteristics:

- Gage thickness, mil or mm, average of the four corners
- Mass, g, to one-hundredth of a gram.

- Length, cm, average of the lengths of the two sides.
- Width, cm, average of the widths of the two ends.

At the end of 30, 60, 90, and 120 days of exposure, remove enough samples from the leachate to determine the membrane's physical properties. Cool the wet specimen in a labeled container of fresh leachate at room temperature for 1 hour before testing. Wipe off the specimen to remove as much waste material as possible, rinse it well with water, and place it in a labeled polyethylene bag to prevent the specimen from drying out. Test the sample within 24 hours of removal from the exposure tank.

To test the immersed sample, wipe off any remaining waste and rinse the sample with deionized water. Blot the specimen dry and measure its thickness, mass, length, and width.

Perform tests 1 through 4 listed above on the exposed specimen to determine any changes in the liner material after exposure to the leachate. Plot the results on a curve for each property over the time period of 0 to 120 days.

APPENDIX B

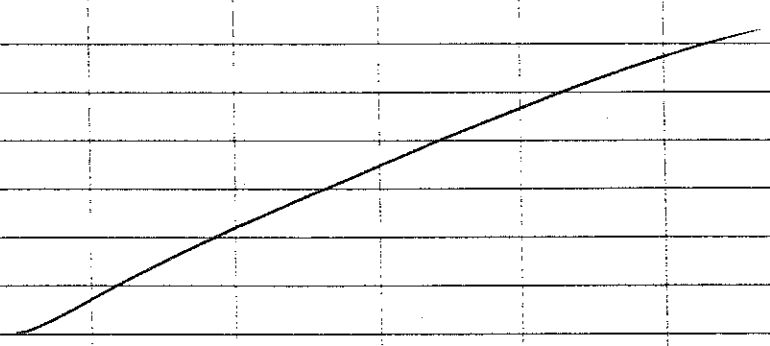
RAW LAB DATA

(LAB BOOK 40024)

Work Performed by: R Higgs Project No. ND751-2464 Date of Work: 8/17/84

Title or Purpose: Tensile properties 30 day exp Continued from: —

		Strength @ break PSI	Elong @ break %	Stress @ elongation of 100% PSI	200% PSI	300% PSI	Strength @ yield PSI
TANK 35 (50 C)	1	2320	232	2210	2320	—	3540
	2	2320	418	2180	2210	2250	3390
	3	2360	395	2180	2180	2280	3390
	4	2540	518	2110	2140	2250	3320
	5	2320	430	2110	2180	2250	3320
	$\bar{x}$	2370	399	2160	2210	2260	3390
	s	95.5	104	45.5	68.4	15.0	89.8
TANK 36	1	2460	480	2210	2250	2280	3460
	2	2540	510	2110	2180	2250	3320
	3	2500	432	2250	2320	2390	3460
	4	2460	382	2250	2320	2390	3460
	5	2460	498	2180	2210	2250	3360
	$\bar{x}$	2480	460	2200	2260	2310	3410
	s	35.8	52.9	58.3	63.5	72.2	67.2



Entered by: R Higgs Date: 8/17/84 Continued to:

Performances of this Work observed by: Disclosed to and understood by me:

Date: Date:

Date: Date:

Work Performed by: R Huggins Project No. N0751-2413 Date of Work: 12/21/84

Title or Purpose: Tensile & Puncture properties - 30 day Continued from: 34

TENSILE TANK 37

	Strength @ break PSI	Elong. @ break %	Stress @ elongations of 100% PSI	200% PSI	300% PSI	Strength @ yield PSI
1	2520	422	2280	2350	2380	3600
2	2310	200	2240	2310	—	3450
3	2550	460	2280	2290	2350	3570
4	2350	260	2280	2350	—	3500
5	2450	212	2410	2450	—	3640
$\bar{x}$	2450	311	2300	2350	2360	3550
s	104	122	65.0	61.6	21.2	76.6

PUNCTURE TANK 37

	Strength @ break lbs	Elong. @ break %	Strength @ yield lbs
1	81	1080	87
2	85	1080	93
3	83	1080	95
4	86	1000	97
5	90	1170	95
$\bar{x}$	850	1080	934
s	3.39	60.2	3.85

Entered by: R Huggins Date: 1/28/85 Continued to: 36

Performances of this work observed by: Disclosed to and understood by me:

Date: Date:

Date: Date:

Work Performed by: R Huggins Project No. N4360-2413 Date of Work: 1/8/85

Title or Purpose: Tensile & Puncture properties - 31 day exp Continued from:

TENSILE		Strength @ break PSI	Elong. @ break %	Stress @ 100% PSI	Elongation @ 200% PSI	Elongation @ 300% PSI	Strength @ yield PSI
TANK 38	1	2760	422	2480	2550	2720	3740
	2	2650	370	2410	2550	2620	3640
	3	2580	77.5	—	—	—	3670
	4	2690	175	2620	—	—	3780
	5	2790	375	2550	2720	2860	3880
	$\bar{x}$	2690	284	2520	2610	2730	3740
	s	84.4	149	90.4	98.1	120	95.0

PUNCTURE		Strength @ break lbs.	Elong. @ break %	Strength @ yield lbs.
	1	87	1080	100
	2	87	1080	99
	3	90	1080	97
	4	86	1000	97
	5	91	1000	105
	$\bar{x}$	88.2	1050	99.6
	s	2.17	43.8	3.29

Entered by: R Huggins Date: 1/28/85 Continued to: 39

Performances of this work observed by: Disclosed to and understood by me:

Date: Date:

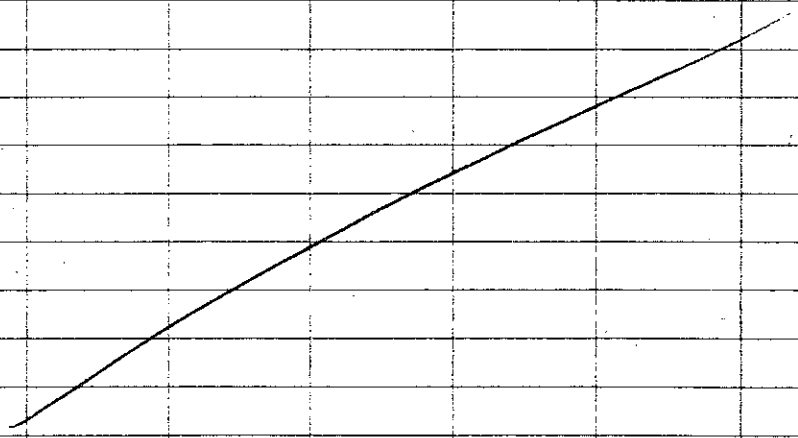
Date: Date:

Work Performed by: R Huggins Project No. N0751-2404 Date of Work: 9/19/84

Title or Purpose: Sample controls - tensile Continued from: —

30 days/101

	Strength @ break PSI	Elong. @ break %	Stress @ 100% PSI	elongations of 200% PSI	300% PSI	Strength @ yield PSI
1	2540	492	2280	2360	2460	3540
2	2610	502	2210	2250	2320	3460
3	2460	498	2280	2360	2460	3460
4	2390	355	2180	2250	2360	3460
5	2460	470	2250	2280	2390	3500
6	2430	445	2250	2360	2390	3500
7	2710	532	2210	2250	2250	3560
8	2460	345	2250	2320	2390	3540
9	2460	442	2280	2320	2360	3570
10	2320	268	2210	2280	—	3430
→ $\bar{x}$	2480	435	2240	2300	2380	3500
s	111	84.9	35.6	46.9	65.4	44.3



Entered by: R Huggins Date: 9/19/84 Continued to: 14

Performances of this work observed by: Disclosed to and understood by me:

Date: Date:

Date: Date:

Work Performed by: R Huggins Project No. N0751-2404 Date of Work: 11/16/84

Title or Purpose: Controls Continued from: —

Tensile	Strength @ break PSI	Elong @ break %	Stress @ 100% PSI	Elongation of 200% PSI	300% PSI	Strength @ yield PSI
1	2540	420	2360	2430	2460	3680
2	2750	502	2390	2460	2540	3750
3	2570	480	2320	2320	2430	3540
4	2680	472	2390	2500	2610	3540
5	2610	380	2430	2500	2540	3710
6	2610	412	2390	2460	2540	3680
7	2710	485	2390	2460	2500	3750
8	2430	188	2390	—	—	3680
9	2460	210	2390	2460	—	3750
10	2610	398	2390	2460	2540	3610
$\bar{X}$	2600	395	2380	2450	2520	3670
s	162	111	28.0 RH	534	558	80.6

Puncture	Strength @ break lbs	Elong @ break %	Strength @ yield lbs.	Strength @ break lbs	Elong @ break %	Strength @ yield lbs.
1	85	702	—	9 87	1140	99
2	74	877	93	10 87	1140	97
3	87	877	94	$\bar{X}$ 83.3	990	96.7
4	81	1050	97	s 3.92	137	224
5	83	1050	99			
6	83	965	97			
7	82	1050	95			
8	84	1050	99			

Entered by: R Huggins Date: 11/26/84 Continued to: —

Performances of this work observed by: Disclosed to and understood by me:

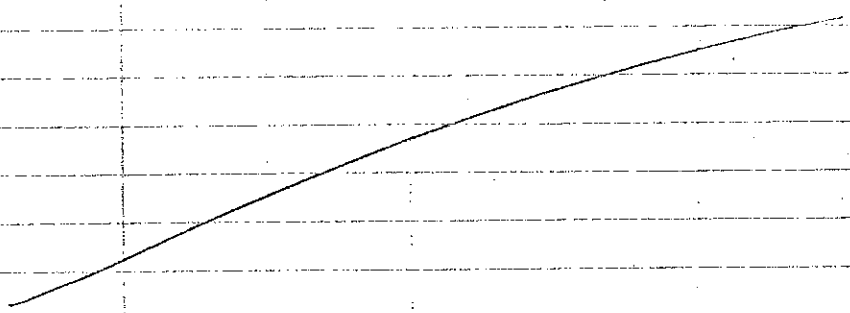
Date: Date:

Date: Date:

Work Performed by: R Hug Project No 10751-204 Date of Work: 9/17/64

Title or Purpose: Tensile properties of dry exp Continued from: —

		Strength along Grain Black	Strength Across Grain Black	Elongation at 10%	Elongation at 20%	Elongation at 30%	Strength at Yield
		PSI	%	PSI	PSI	PSI	PSI
TRK 35	1	2610	515	2250	2280	2340	3540
	2	2540	508	2280	2360	2390	3610
	3	2390	402	2210	2250	2320	3500
	4	2340	405	2250	2250	2320	3540
	5	2680	542	2280	2320	2360	3570
	X	2530	474	2250	2290	2360	3550
	S	132	66.0	28.3	47.6	35.1	41.9
TRK 36	1	2460	505	2250	2250	2320	3490
	2	2390	400	2250	2250	2320	3540
	3	2540	465	2250	2320	2340	3490
	4	2540	500	2320	2340	2460	3610
	5	2320	343	2240	2210	2230	3320
	X	2450	444	2220	2280	2350	3450
	S	95.9	67.9	68.9	71.3	71.3	108



Entered by: R Hug Date: 9/17/64 Continued to: —

Performances of this work observed by: Disclosed to and understood by me.

Date: Date:

Date: Date:

Work Performed by: R Lhuggs Project No. M4360-2413 Date of Work: 1/22/85

Title or Purpose: Puncture & Tensile ~~Propert~~ Properties -62 day exp Continued from: —

TENSILE

		Strength @ break PSI	Elong @ break %	Stress @ 100% PSI	elongations of 200% PSI	300% PSI	Strength @ yield PSI
TANK 37	1	2410	335	2310	2350	2410	3640
	2	2480	152	2480	—	—	3710
	3	2380	230	2310	2380	—	3640
	4	2410	165	2380	—	—	3780
	5	2890	488	2410	2450	2520	3710
	$\bar{X}$	2510	274	2380	2390	2460	3700
	s	213	140	71.9	51.3	77.8	58.6

PUNCTURE

		Strength @ break lbs	Elong @ break %	Strength @ yield lbs
	1	89	1000	102
	2	83	1000	95
	3	86	1000	95
	4	83	1000	99
	5	81	1000	94
$\bar{X}$	~~6~~	84.4	1000	97.0
s	~~7~~	3.13	0	3.39
	~~8~~			
	~~9~~			
	~~10~~			
	~~11~~			
	~~12~~			

Entered by: R Lhuggs Date: 1/28/85 Continued to: 42

Performances of this work observed by: Disclosed to and understood by me:

Date: Date:

Date: Date:

Work Performed by: R Huggs Project No. N0751-243 Date of Work: 2/5/85

Title or Purpose Puncture & Tensile properties 60 day exp Continued from: —

TENSILE

	Strength @ break lbs. PSI	Elong @ break %	Stress @ 100% lbs PSI	Elongation of 200% lbs PSI	300% lbs PSI	Strength @ yield lbs PSI
TANK 38 1	2520	492	2210	2280	2310	3570
2	2280	210	2210	2280	—	3540
3	2280	210	2210	2280	—	3540
4	2350	~~225~~ 125	2280	—	—	3370
5	2380	182	2350	—	—	3710
$\bar{x}$	2360	244	2250	2280	—	3550
s	98.6	143	62.6	0	—	121

PUNCTURE

	Strength @ break lbs.	Elong. @ break %	Strength @ yield lbs
1	83	917	97
2	77	917	93
3	83	917	99
4	78	1000	97
5	76	833	93
$\bar{x}$	79.4	917	95.8
s	3.36	59.0	2.68

Entered by: R Huggs Date: 2/6/85 Continued to: —

Performances of this work observed by: Disclosed to and understood by me:

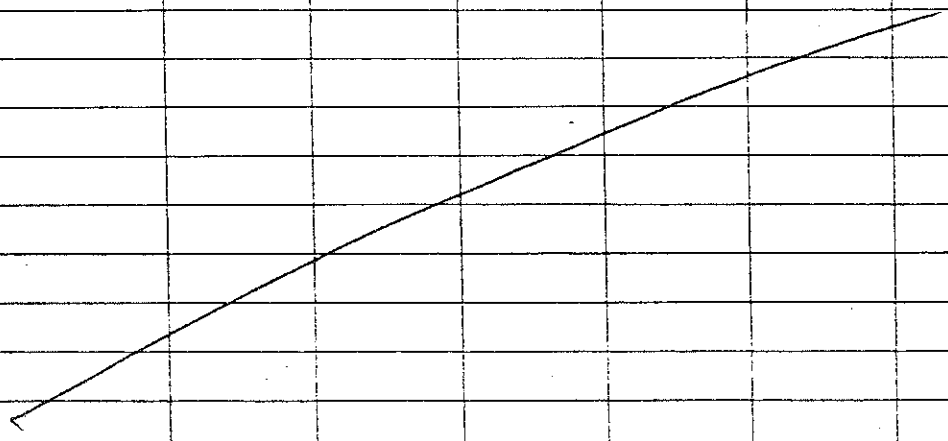
Date: Date:

Date: Date:

Work Performed by: R Huggins Project No. NO751-2404 Date of Work: 10/17/84 RA

Title or Purpose: Tensile properties - 91 day exp Continued from: —

		Strength @ break PSI	Elong. @ break %	Stress @ elongation of 100% PSI	200% PSI	300% PSI	Strength @ yield PSI
✓							
TANK 35	1	2680	445	2320	2320	2320	3610
	2	2570	290	2390	2460	—	3680
	3	2610	430	2280	2390	2540	3570
	4	2390	145	2390	—	—	3540
	5	2610	425	2390	2430	2460	3610
	$\bar{x}$	2570	347	2350	2400	2440	3600
	s	109	129	51.3	60.6	111	52.6
TANK 36	1	2680	490	2320	2360	2390	3570
	2	2860	538	2250	2280	2390	3430
	3	2500	290	2390	2390	—	3610
	4	2320	108	2320	—	—	3570
	5	2390	148	2320	—	—	3540
	$\bar{x}$	2550	315	2320	2340	2390	3540
	s	220	195	49.5	56.9	0	68.4



Entered by: R Huggins Date: 10/23/84 Continued to: —

Performances of this work observed by: Disclosed to and understood by me:

Date: Date:

Date: Date:

Work Performed by: R Huggins Project No. N075-2413 Date of Work: 2/20/85

Title or Purpose: Puncture & Tensile properties - tank 37, 90 day Continued from: —

TENSILE TANK 37	Strength @ break PSI	Elong. @ break %	Stress @ elongations of 100% PSI	200% PSI	300% PSI	Strength @ yield PSI
1	2480	110	2410	—	—	3780
2	2350	342	2310	2350	2350	3670
3	2310	232	2240	2280	—	3540
4	2280	105	2240	2280	—	3570
5	2380	248	2350	2350	—	3640
$\bar{x}$	2360	207	2310	2320	—	3640
s	77.1	100	73.1	40.4	—	94.1

PUNCTURE TANK 37	Strength @ break lbs.	Elong. @ break %	Strength @ yield lbs
1	83	1000	95
2	82	1000	95
3	85	917	98
4	87	1000	96
5	93	1000	101
$\bar{x}$	86.0	983	97.0
s	4.36	37.1	2.55

Entered by: R Huggins Date: 2/20/85 Continued to: —

Performances of this work observed by: Disclosed to and understood by me:

Date: Date:

Date: Date:

Work Performed by: R Huggins Project No. N0751-2413 Date of Work: 3/7/85

Title or Purpose: Tensile & puncture properties - 90 day exp Continued from: —

TENSILE TANK 38	Strength @ break PSI	Elong. @ break %	Stress @ 100% PSI	Elongations of 200% PSI	300% PSI	Strength @ yield PSI
1	2620	280	2550	2620	—	3880
2	2690	328	2620	2690	2690	3910
3	2760	422	2520	2650	2620	3840
4	2520	150	2480	—	—	3740
5	2960	480	2550	2620	2620	3880
$\bar{x}$	2710	332	2540	2640	~~33.2~~ 2640	3850
s	166	128	51.3	33.2	40.4	66.3

PUNCTURE TANK 38	Strength @ break lbs.	Elong. @ break %	Strength @ yield lbs.
1	84	~~968~~ 1000	102
2	86	~~968~~ 1000	103
3	87	~~968~~ 1000	102
4	89	~~887~~ 917	106
5	86	~~968~~ 1000	104
$\bar{x}$	86.4	983	103
s	1.82	37.1	1.67

Entered by: R Huggins Date: 3/7/85 Continued to: —

Performances of this work observed by:	Disclosed to and understood by me:
Date:	Date:
Date:	Date:

Work Performed by: R Huggins Project No. N0751-2404 Date of Work: 10/17/84

Title or Purpose: Tensile control Continued from: —

		Strength @ break PSI	Elong @ break %	Stress @ elongations of 100% PSI	200% PSI	300% PSI	Strength @ yield PSI
~~RH~~							
	1	2540	170	2460	—	—	3640
	2	2890	542	2610	2610	2080	3960
	3	2540	335	2430	2460	2540	3680
90 day	4	2610	425	2390	2460	2540	3460
	5	2680	458	2460	2500	2540	3680
	6	2680	438	2460	2460	2540	3750
	7	2540	368	2320	2430	2460	3500
	8	2640	458	2320	2320	2390	3610
	9	2680	465	2390	2430	2460	3540
	10	2570	448	2360	2460	2500	3570
	$\bar{x}$	2640	411	2420	2460	2520	3640
	s	107	101	85.9	75.4	80.3	144

$\bar{x}$ & s including controls on p. 13 in calculations

$\bar{x}$	2560	423	2330	2380	2450	3570
s	132	91.8	112	100	102	127

Entered by: R Huggins Date: 10/23/84 Continued to: —

Performances of this work observed by: Disclosed to and understood by me:

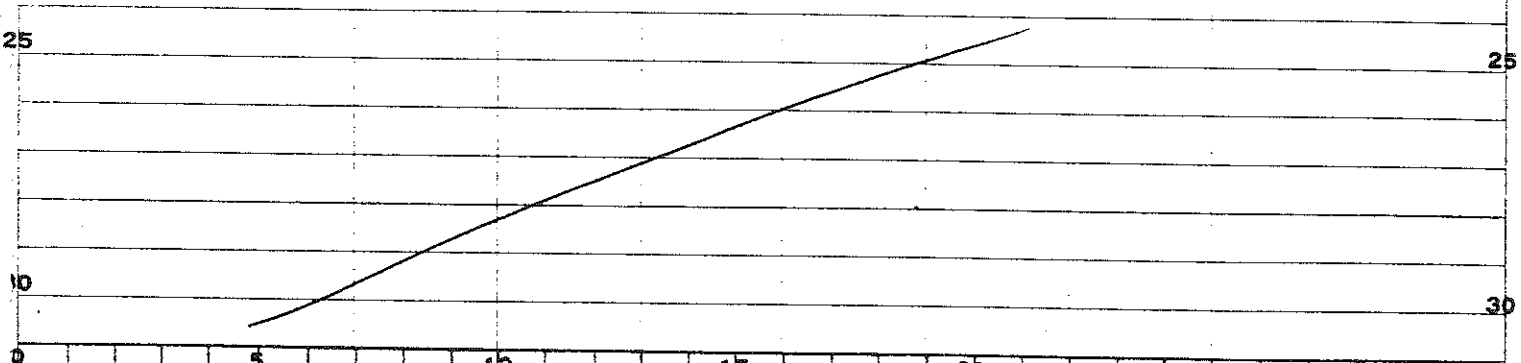
Date: Date:

Date: Date:

Work Performed by: R Hugg Project No. N0751-2404 Date of Work: 11/16/84

Title or Purpose: Tensile properties - 121 day exp Continued from:

		Strength @ break PSI	Elong @ break %	Stress @ elongations of 100% PSI	200% PSI	300% PSI	Strength @ yield PSI
TANK 35	1	2610	315	2390	2500	2610	3610
	2	2460	270	2390	2460	—	3750
	3	2640	460	2320	2320	2390	3640
	4	2540	280	2360	2460	—	3680
	5	2320	180	2280	—	—	3500
	6	2540	465	2250	2280	2320	3540
	7	2500	505	2180	2280	2360	3390
	8	2500	492	2250	2280	2430	3460
	9	2460	420	2180	2250	2320	3460
	10	2430	420	2250	2320	2320	3540
	11	2390	405	2210	2250	2250	3500
	12	2610	468	2250	2390	2540	3360
	13	2460	355	2210	2320	2390	3540
	14	2390	408	2250	2280	2320	3610
	15	2430	512	2320	2390	2390	3500
→	X	2480	397	2270	2340	2390	3540
	S	90.6	97.9	69.3	83.7	101	106



Entered by: R Hugg Date: 11/26/84 Continued to: —

Performances of this work observed by: Disclosed to and understood by me:

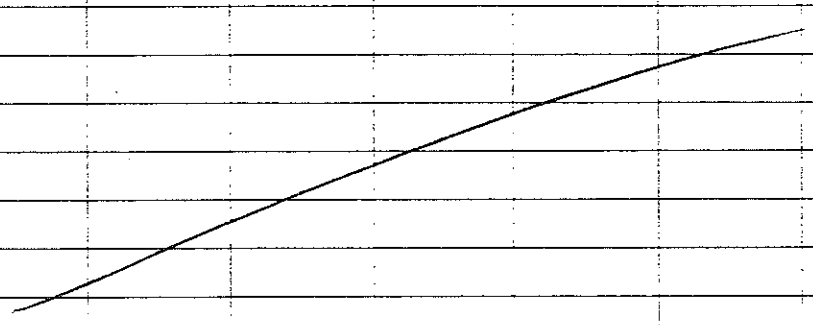
Date: Date:

Date: Date:

Work Performed by: R Hugg Project No. 10751-2404 Date of Work: 11/16/84

Title or Purpose: Tensile properties - 121 day exp. Continued from:

		Strength @ break PSI	Elong. @ break %	Stress @ elongations of 100% PSI	200% PSI	300% PSI	Strength @ yield PSI
TANK 36	1	2460	418	2250	2320	2320	3570
	2	2390	415	2180	2210	2285	3320
	3	2500	240	2280	2460	—	3460
	4	2460	470	2250	2320	2390	3460
	5	2570	505	2210	2250	2360	3460
	6	2460	420	2210	2250	2390	3430
	7	2390	400	2180	2250	2320	3430
	8	2430	410	2210	2250	2320	3460
	9	2930	555	2180	2210	2250	3390
	10	3180	590	2180	2210	2210	3390
	11	2540	485	2180	2210	2280	8360
	12	2780	505	2320	2320	2320	3500
	13	3040 RH	570	2110	2180	2210	3360
	14	2540	490	2140	2180	2250	3320
	15	2320	495	2070	2110	2180	3210
	X	2600	464	2200	2250	2290	3410
	S	260	86.4	63.5	82.2	66.0	87.2



Entered by: R Hugg Date: 11/26/84 Continued to: 22

Performances of this work observed by: Disclosed to and understood by me:

Date: Date:

Date: Date:

Work Performed by: R Huggs Project No. N0751-2/13 Date of Work: 3/21/85

Title or Purpose: Tensile properties - tank 37 - 120 day exp Continued from: —

TANK 37	Strength @ break PSI	Elong @ break %	Stress @ elongations of 100% PSI	200% PSI	300% PSI	Strength @ yield PSI
1	2480	158	2410	—	—	3780
2	2410	158	2380	—	—	3780
3	2350	235	2280	2350	—	3570
4	2410	160	2350	—	—	3640
5	2350	118	2350	—	—	3670
6	2410	140	2350	—	—	3640
7	2410	168	2410	—	—	3740
8	2690	455	2410	2450	2450	3780
9	2480	360	2280	2350	2550	3570
10	2480	470	2280	2350	2380	3540
11	2280	150	2210	—	—	3440
12	2350	220	2280	2350	—	3600
13	2410	170	2380	—	—	3740
14	2380	255	2310	2350	—	3640
15	2280	182	2280	—	—	3570
$\bar{x}$	2410	227	2330	2370	2460	3650
s	99.5	113	61.3	40.8	85.4	102

Entered by: R Huggs Date: 3/22/85 Continued to: 54

Performances of this work observed by: Disclosed to and understood by me:

Date: Date:

Date: Date:

Work Performed by: R Huggs — Project No. N0751-2413 Date of Work: 4/5/85

Title or Purpose: Tenaik properties - tank 38 119 day exp Continued from: —

	Strength @ break PSI	Elong. @ break %	Stress @ elongations of 100% PSI	200% PSI	300% PSI	Strength @ yield PSI
1	2480	102	2480	—	—	3840
2	2580	365	2480	2580	2620	3880
3	2580	392	2380	2480	2550	3840
4	2620	190	2580	—	—	3980
5	2550	422	2410	2410	2480	3740
6	2550	165	2410	—	—	3470
7	2480	350	2410	2450	2480	3810
8	2690	212	2580	2690	—	3910
9	2550	132	2580	—	—	3810
10	2690	220	2690	2690	—	3780
11	2820	405	2550	2620	2620	3910
12	2720	330	2580	2620	2690	3910
13	2620	87.5	—	—	—	3810
14	2760	360	2690	2760	2860	3840
15	2410	128	2410	—	—	3640
$\bar{x}$	2610	257	2520	2590	2614	3810
s	113	121	105	120	133	124

Entered by: R Huggs Date: 4/8/85 Continued to: —

Performances of this work observed by:	Disclosed to and understood by me:
Date:	Date:
Date:	Date:

Work Performed by: R Huggins Project No. N0751-2404 Date of Work: 11/16/84

Title or Purpose: Controls Continued from: —

Tensile

	Strength @ break PSI	Elong @ break %	Stress @ elongation of 100% PSI	200% PSI	300% PSI	Strength @ yield PSI
1	2540	420	2360	2430	2460	3680
2	2750	502	2390	2460	2540	3750
3	2570	480	2320	2320	2430	3540
4	2680	472	2390	2500	2610	3540
5	2610	380	2430	2500	2540	3710
6	2610	412	2390	2460	2540	3680
7	2710	485	2390	2460	2500	3750
8	2430	188	2390	—	—	3680
9	2460	210	2390	2460	—	3750
10	2610	398	2390	2460	2540	3610
$\bar{x}$	2600	395	2380	2450	2520	3670
s	162	111	28.0 RH	53.4	55.8	80.6

120 day

Puncture

	Strength @ break lbs	Elong @ break %	Strength @ yield lbs		Strength @ break lbs	Elong @ break %	Strength @ yield lbs
1	85	702	—	9	87	1140	99
2	74	877	93	10	87	1140	97
3	87	877	94	$\bar{x}$	83.3	990	96.7
4	81	1050	97	s	3.92	137	224
5	83	1050	99				
6	83	965	97				
7	82	1050	95				
8	84	1050	99				

Entered by: R Huggins Date: 11/26/84 Continued to: —

Performances of this work observed by: Disclosed to and understood by me:

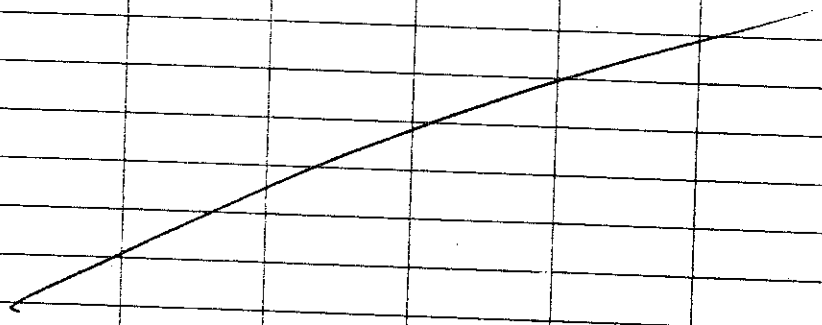
Date: Date:

Date: Date:

Work Performed by: R Hugg — Project No. 0751-204 Date of Work: 8/17/84

Title or Purpose: Puncture properties 30 day exp Continued from: —

		Strength @ break (lbs)	Elong. @ break (%)	Strength @ yield (lbs)
TANK 35	1	83	1050	93
	2	83	1050	95
	3	83	1140	93
	4	85	1050	97
	5	83	1050	92
	$\bar{x}$	83.4	1070	94.0
	s	0.894	40.2	2.00
TANK 36	1	80	1050	90
	2	79	1140	87
	3	83	1140	91
	4	83	1050	91
	5	79	965	91
	$\bar{x}$	80.8	1070	90.0
	s	2.05	73.5	1.73



Performed by: R Hugg Date: 8/17/84 Continued to:

Performances of this work observed by: Disclosed to and understood by me:

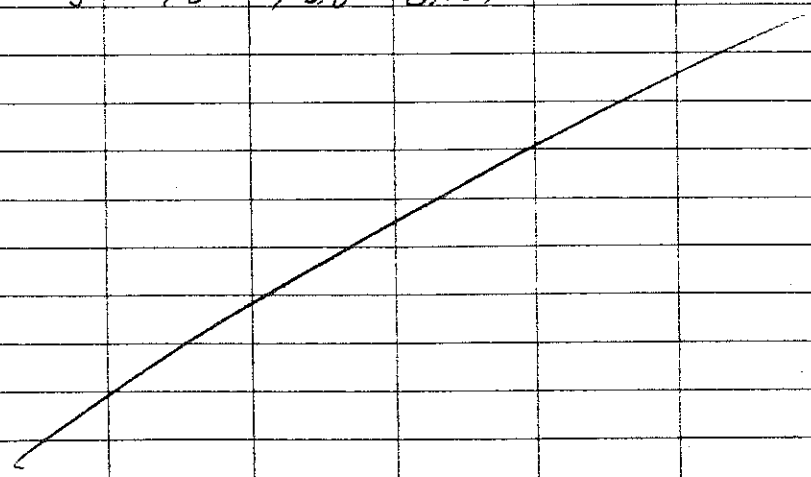
Date: Date:

Date: Date:

Work Performed by: R Hugg Project No. ND751-2404 Date of Work: 9/19/84

Title or Purpose: Sample controls - puncture Continued from: 13

	Strength @ break lbs	Elong. @ break %	Strength @ yield lbs.
1	73	965	87
2	71	965	85
3	75	1050	88
4	71	1050	83
5	74	877	85
6	76	965	91
7	77	1146	91
8	76	1050	91
9	76	965	89
10	81	1050	93
$\bar{x}$	75.0	1010	88.3
s	2.98	73.8	3.27



Recorded by: R Hugg Date: 9/19/84 Continued to: —

Performances of this work observed by:	Disclosed to and understood by me:
Date:	Date:
Date:	Date:

Work Performed by: R Huggins Project No. N075-2404 Date of Work: 10/17/84

Title or Purpose: Puncture controls Continued from: —

	Strength @ break lbs.	Elong. @ break %	Strength @ yield lbs.
1	95	1230	93
2	90	1140	95
3	89	1140	96
4	89	1230	97
5	86	1140	93
6	88	1230	96
7	87	1140	95
8	87	1140	96
9	86	1140	96
10	86	1050	95
$\bar{X}$	88.3	1160	95.2
s	2.75	56.9	1.32
$\bar{X}$ & s including controls on p. 4 in calculations			
$\bar{X}$	81.6	1080	91.8
s	7.37	100	4.29

Entered by: R Huggins Date: 10/23/84 Continued to: —

Performances of this work observed by: Disclosed to and understood by me:

Date: Date:

Date: Date:

Work Performed by: R H[illegible] Project No. [illegible] Date of Work: 9/17/84

Title or Purpose: Puncture properties - 6 day exp Continued from: —

		Strength Chuck lbs	Elong Chuck %	Strength Grid lbs
Tank 35	1	80	1140	91
	2	83	1140	91
	3	79	1050	85
	4	79	1050	83
	5	78	1140	85
	$\bar{x}$	79.8	1100	87.0
	s	1.92	49.3	3.74
Tank 36	1	85	1140	92
	2	84	1140	91
	3	84	1230	91
	4	83	1230	89
	5	83	1230	90
	$\bar{x}$	83.8	1194	90.6
	s	0.837	49.3	1.14

Entered by: R H[illegible] Date: 9/17/84 Continued to: —

Performances of this work observed by: Disclosed to and understood by me:

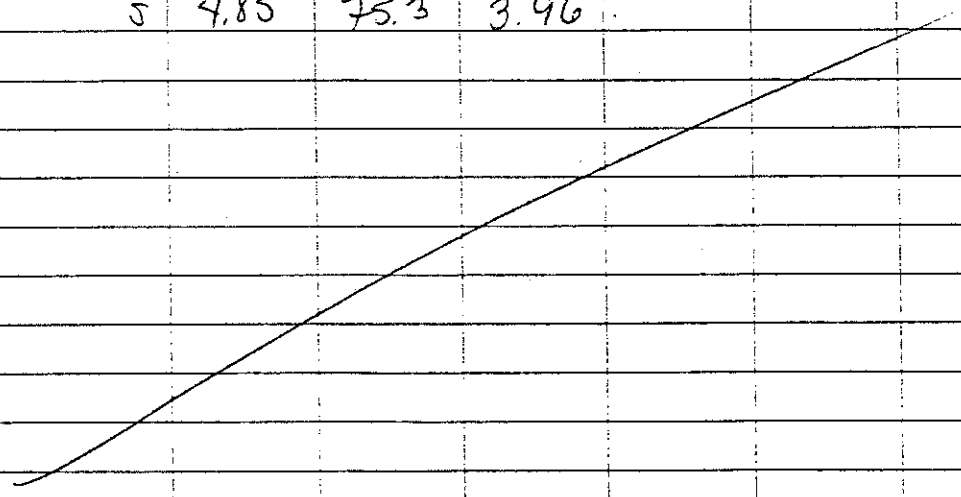
Date: Date:

Date: Date:

Work Performed by: R Huggs Project No. N0751-2404 Date of Work: 10/17/84

Title or Purpose: Puncture properties - 91 day exp. Continued from: —

		Strength @ break lbs	Elong. @ break %	Strength @ yield lbs.
TANK 35	1	88	1140	96
	2	81	1050	92
	3	87	1050	95
	4	85	1140	90
	5	87	1140	92
	$\bar{x}$	85.6	1100	93.0
	s	2.79	49.3	2.45
TANK 36	1	76	1050	84
	2	84	1140	91
	3	85	1140	94
	4	89	1230	93
	5	86	1230	92
	$\bar{x}$	84.0	1160	90.8
	s	4.85	75.3	3.96



Entered by: R Huggs Date: 10/23/84 Continued to: —

Performances of this work observed by: Disclosed to and understood by me:

Date:	Date:
Date:	Date:

Work Performed by: R Hugg Project No. N0751-2404 Date of Work: 11/16/84

Title or Purpose: Puncture properties - 121 day exp Continued from: —

		Strength @ break lbs.	Elong. @ break %	Strength @ yield lbs
TANK 35	1	83	1050	91
	2	82	965	95
	3	81	1050	87
	4	90	1140	95
	5	85	1050	97
	6	83	1050	93
	7	83	1050	96
	8	86	1140	94
	9	83	1050	95
	10	81	965	95
	11	77	1050	89
	12	79	965	95
	13	83	1050	95
	14	80	1050	93
	15	89	965	91
	$\bar{X}$	83.0	1040	93.4
	s	3.46	55.7	2.77

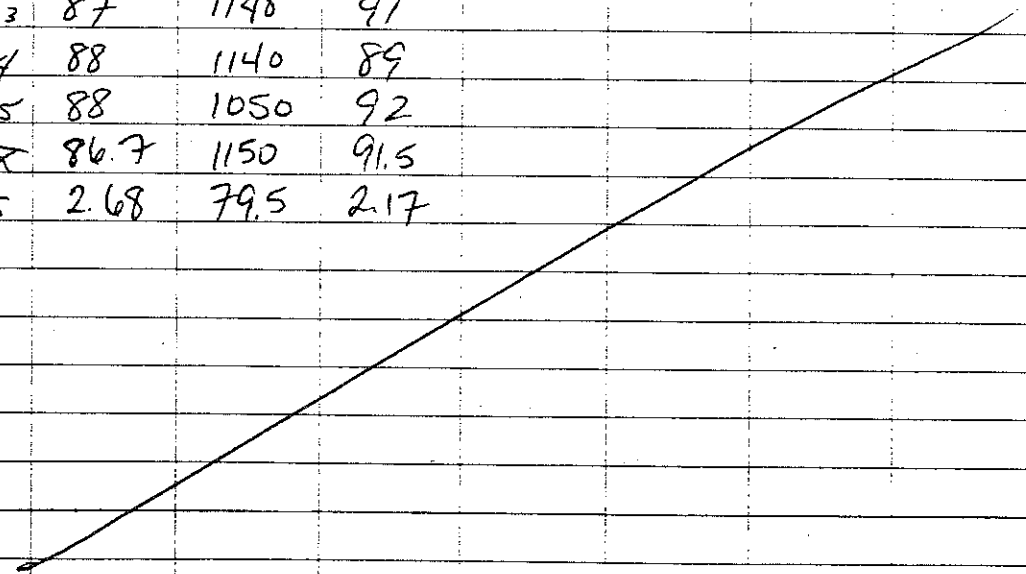
Entered by: R Hugg Date: 11/26/84 Continued to: 24

Performances of this work observed by:	Disclosed to and understood by me:
Date:	Date:
Date:	Date:

Work Performed by: R Huggins Project No. N0751-240f Date of Work: 11/16/84

Title or Purpose: Puncture properties - 121 day exp Continued from: 23

		Strength @ break lbs.	Elong @ break %	Strength @ yield lbs.
TANK 36	1	81	1050	91
	2	83	1050	91
	3	85	1050	93
	4	89	1140	95
	5	91	1230	95
	6	87	1230	91
	7	89	1230	91
	8	83	1050	89
	9	87	1140	95
	10	87	1230	89
	11	89	1230	92
	12	87	1230	89
	13	87	1140	91
	14	88	1140	89
	15	88	1050	92
	$\bar{x}$	86.7	1150	91.5
	s	2.68	79.5	2.17



Entered by: R Huggins Date: 11/26/84 Continued to: —

Performances of this work observed by: Disclosed to and understood by me:

Date: Date:

Date: Date:

Work Performed by: R Hugg — Project No. N0751-24/13 Date of Work: 3/21/85

Title or Purpose: Puncture properties - tank 37 - 120 day exp — Continued from: 53

TANK 37	Strength @ break lbs.	Elong. @ break %	Strength @ yield lbs.
1	86	1080	96
2	83	1000	93
3	91	1000	93
4	88	1000	102
5	86	1080	97
6	84	1000	97
7	89	1000	103
8	85	917	99
9	92	1000	106
10	85	1000	101
11	83	1000	95
12	84	1000	100
13	87	1000	97
14	88	1080	99
15	89	1000	103
$\bar{x}$	86.7	1010	98.7
s	2.79	41.8	3.81

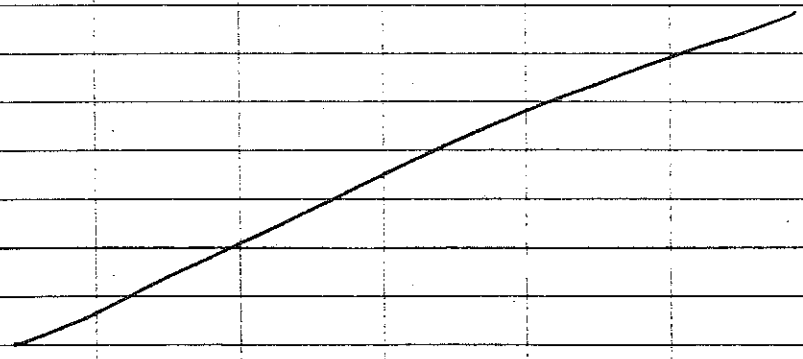
Entered by: R Hugg — Date: 3/22/85 — Continued to: —

Performances of this work observed by:	Disclosed to and understood by me:
Date:	Date:
Date:	Date:

Work Performed by: R Huggins Project No. N0751-2484 Date of Work: 8/17/84

Title or Purpose: Sorption properties 30 day exp. Continued from: —

		Sample wgt (g)	Initial wgt (g)	Weight change (g)	% change (%)
Viking TANK 35	1	1.8975	1.8894	0.0081	0.43
	2	1.8692	1.8445	0.0247	1.34
	3	1.8615	1.8660	-0.0045	0.24
	4	1.8825	1.8851	-0.0026	0.14
	5	1.8936	1.9044	-0.0108	0.567
	$\bar{x}$			0.0030	0.543
	s			0.014	0.475
TANK 36	1	1.8954	1.8767	0.0187	0.996
	2	1.8506	1.8482	0.0024	0.13
	3	1.8721	1.8410	0.0311	1.69
	4	1.8912	1.8619	0.0293	1.57
	5	1.9104	1.8721	0.0383	2.04
	$\bar{x}$			0.0240	0.981
	s			0.014	0.84



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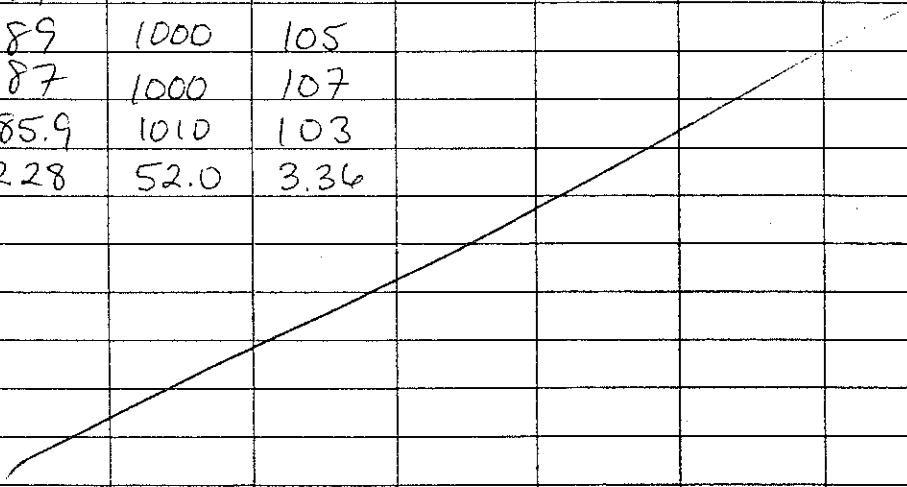
Performances of this work observed by:	Disclosed to and understood by me:
Date:	Date:
Date:	Date:

Work Performed by: R Huggins Project No. N0751-2413 Date of Work: 4/5/85

T or Purpose: Puncture properties - tank 38 119 day exp Continued from: —

	Strength @ break lbs.	Elong. @ break %	Strength @ yield lbs.
1	85	1000	97
2	89	1000	101
3	85	917	103
4	83	917	103
5	83	1000	103
6	85	1000	104
7	89	1080	107
8	86	1080	99
9	87	1000	107
10	89	1000	107
11	83	1080	99
12	85	1000	106
13	84	1080	100
14	89	1000	105
15	87	1000	107
$\bar{x}$	85.9	1010	103
s	228	52.0	3.36



Entered by: R Huggins Date: 4/8/85 Continued to: —

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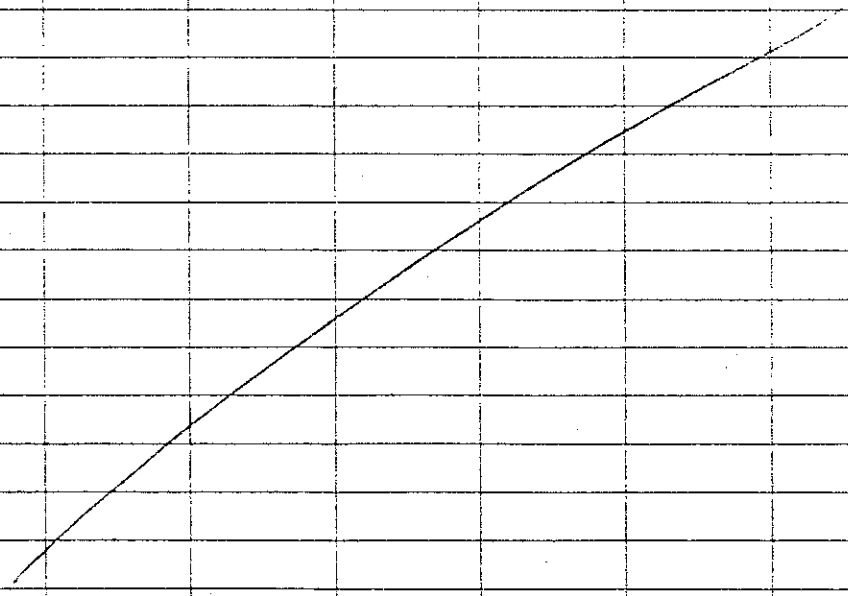
Work Performed by: R Huggins Project No. N0751-2413 Date of Work: 12/21/84

Title or Purpose: Sorption properties - tank 37 30day Continued from: —

		Sample wgt (g)	Initial wgt (g)	Weight change (g)	% change (%)
TANK 37	1	1.9300	~~1.9300~~	0.0360	1.90
	2	1.9012	~~1.9012~~	0.0450	2.42
	3	1.9631	1) 1.8940	0.0515	2.69
	4	1.9431	2) 1.8562	0.0427	2.25
	5	1.9133	3) 1.9116	0.0601	3.24
	X		4) 1.9004	0.0471	2.50
	5		5) 1.8532	0.0092	0.503



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Performances of this work observed by: Disclosed to and understood by me:

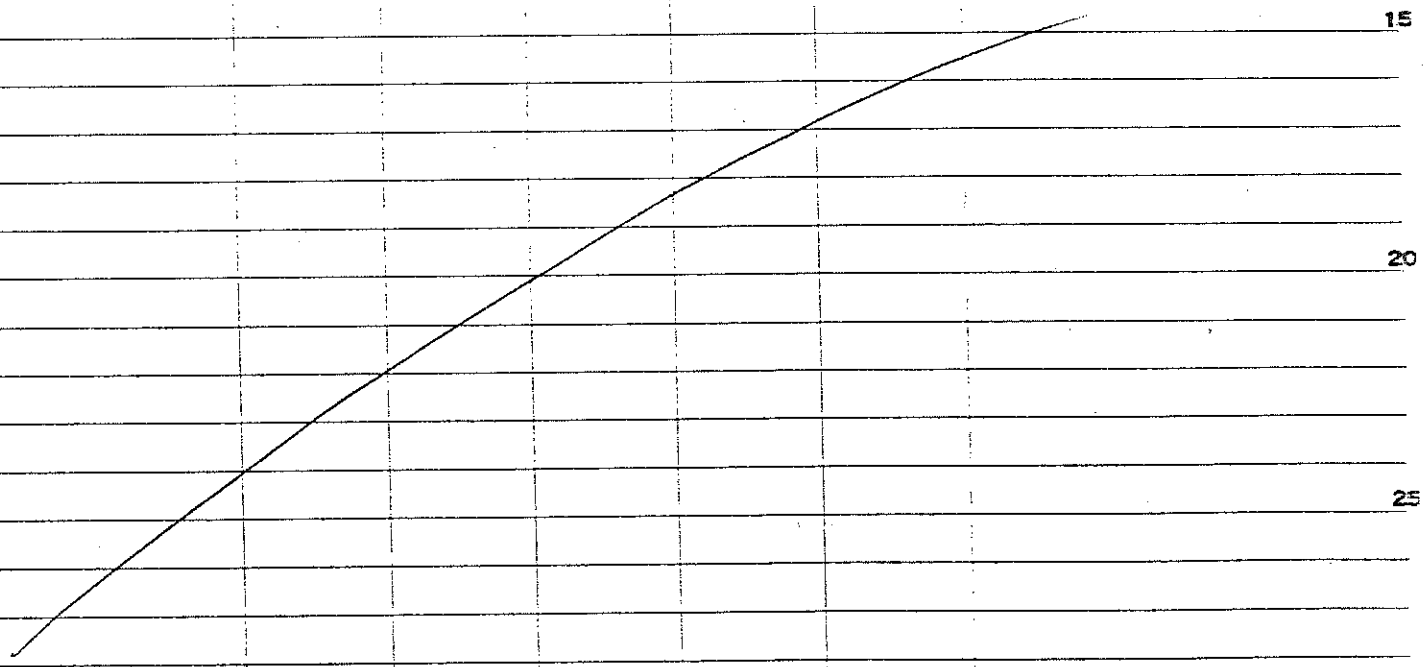
Date: Date:

Date: Date:

Work Performed by: R Huggins Project No. N4360-2413 Date of Work: 1/7/85

Title or Purpose: Sorption properties - 31 day exp. Continued from: —

		Sample wgt g	Initial wgt. g	Weight change g	% change %	
TANK 38	1	1.9551	1.9362	0.0189	0.976	
	2	1.8892	1.8715	0.0177	0.946	
	3	1.8973	1.8794	0.0179	0.952	
	4	1.8849	1.8668	0.0181	0.970	
	5	1.9063	1.8877	0.0186	0.985	0.97 was replaced
	$\bar{x}$			0.0182	0.966	
	s			0.000498	0.0164	



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Performances of this work observed by: Disclosed to and understood by me:

Date: Date:

Date: Date:

Work Performed by: [illegible] Project No. 10751-264 Date of Work: 9/17/84

Title or Purpose: Sorption properties - Cat dairy Continued from: —

	Sample wgt g	Initial wgt g	Weight change g	% change %
Tank 35	6	1.8689	1.8422	0.0267	1.45
	7	1.9205	1.8811	0.0394	2.10
	8	1.9202	1.8854	0.0348	1.85
	9	1.9215	1.8873	0.0342	1.81
	10	1.9075	1.8757	0.0318	1.70
	$\bar{X}$			0.0334	1.78
	s			0.0046	0.236
Tank 36	6	1.8539	1.8434	0.0105	0.570
	7	1.8922	1.8941	-0.0019	0.10
	8	1.8973	1.8945	0.0028	0.15
	9	1.8987	1.8974	0.0013	0.069
	10	1.8863	1.8838	0.0025	0.13
	$\bar{X}$			0.0030	0.20
	s			0.0046	0.21

Entered by: [illegible] Date: 9/17/84 Continued to: —

Performances of this work observed by: Disclosed to and understood by me:

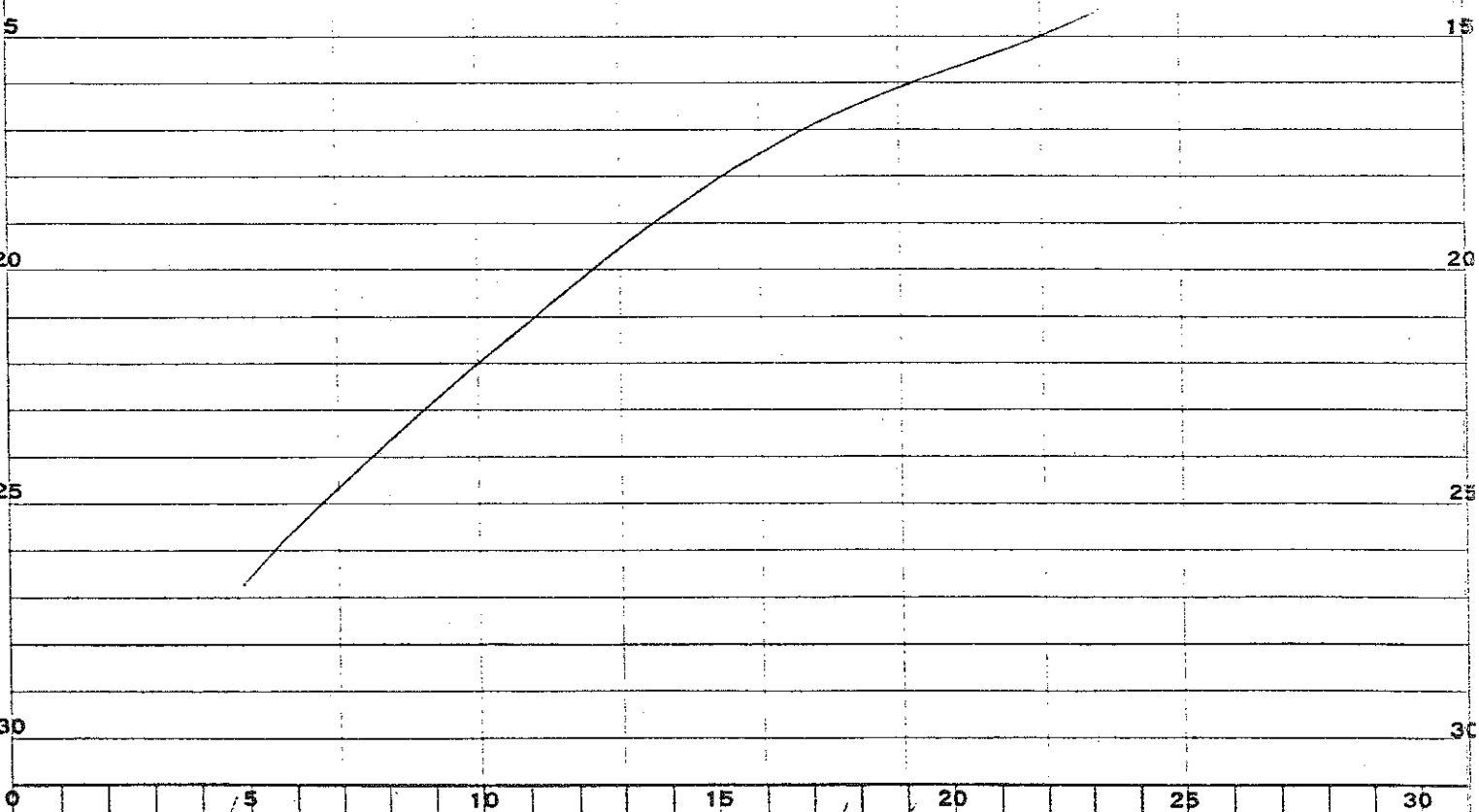
Date: Date:

Date: Date:

Work Performed by: R Huggins Project No. N4360-2413 Date of Work: 1/22/85

Title or Purpose: Sorption data - 62 day exp. Continued from:

		Sample wgt (g)	Initial wgt (g)	Weight change (g)	% change (%)
TANK 37	6	1.9476	1.8936	0.0540	2.85
	7	1.9156	1.8553	0.0603	3.25
	8	1.9136	1.8555	0.0581	3.13
	9	1.9482	1.8875	0.0607	3.22
	10	1.9153	1.8564	0.0589	3.17
	$\bar{x}$			0.0584	3.12
	s			0.00267	0.160



Entered by: R Huggins Date: 1/28/85 Continued to: —

Performances of this work observed by: Disclosed to and understood by me:

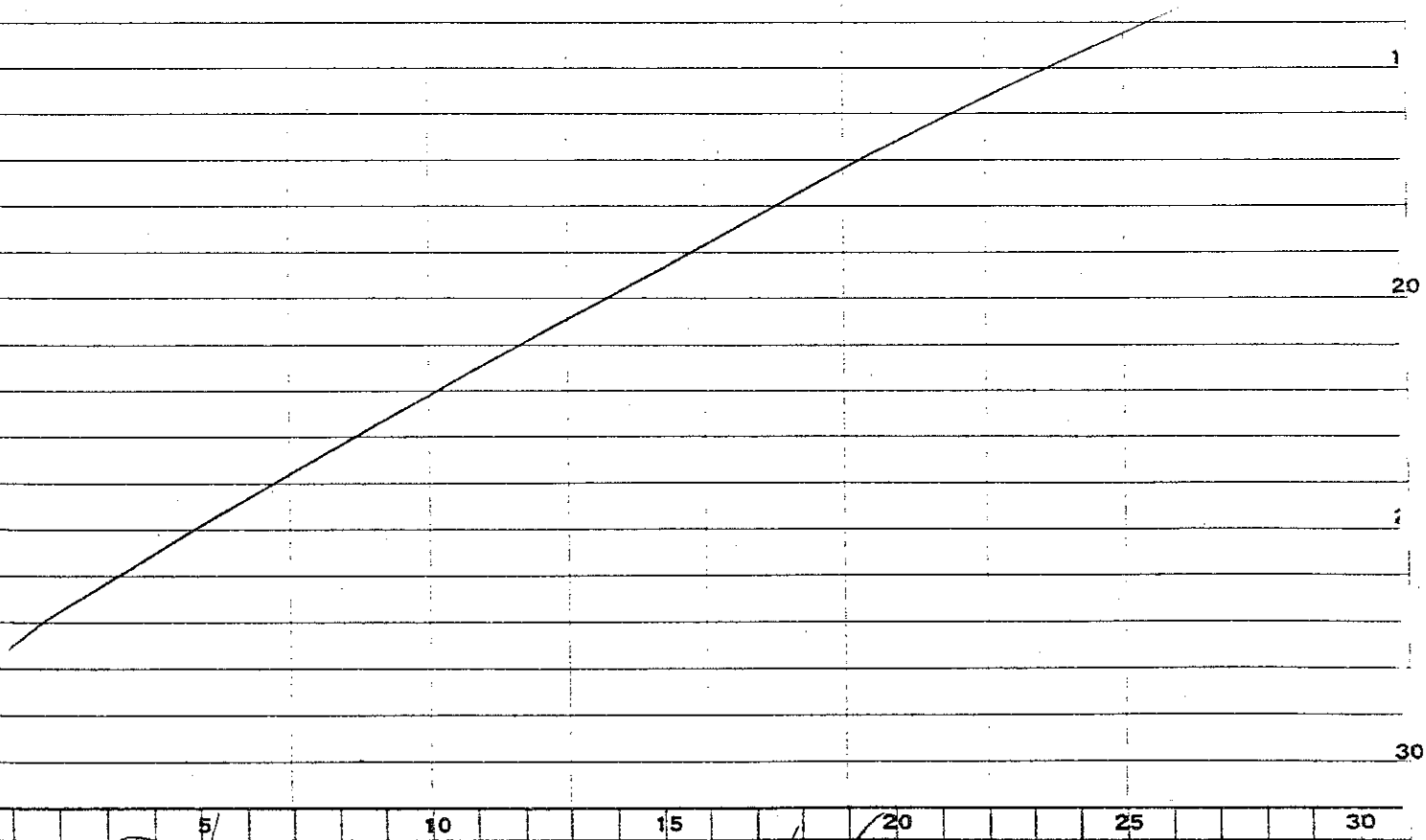
Date: Date:

Date: Date:

Work Performed by: R Huggins Project No. N0751-2413 Date of Work: 2/5/85

Title or Purpose: Sorption properties test 38 60 day Continued from:

	Sample	Initial wgt g	Weight change g	% change %
6	1.9278	1.9112	0.0166	0.868
7	1.8493	1.8325	0.0168	0.917
8	1.9303	1.9131	0.0172	0.899
9	1.8407	1.8241	0.0166	0.910
10	1.9312	1.9144	0.0168	0.878
$\bar{x}$			0.0168	0.894 replaced 0.89
s			0.00024	0.0209



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Performances of this work observed by: Disclosed to and understood by me:

Date: Date:

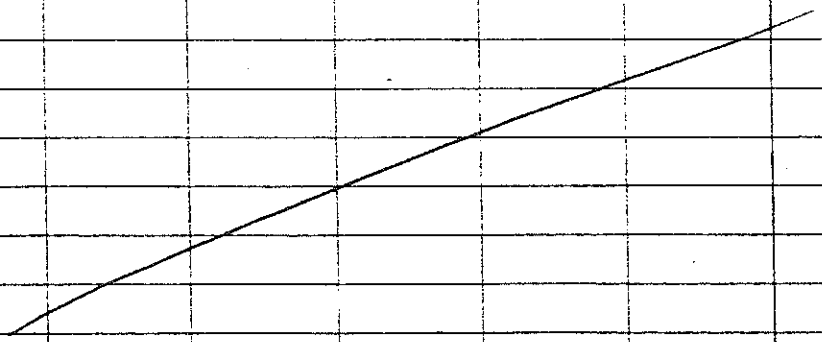
Date: Date:

Work Performed by: R Huggins Project No. N0751-2404 Date of Work: 10/17/84

Title or Purpose: Sorption properties - 91 day exp. Continued from:

		Sample wgt g	Initial wgt g	Weight change g	% change %
Tank 35	11	1.9123	1.8523	0.0600	3.24
	12	1.9202	1.8742	0.0460	2.45
	13	1.9095	1.9027	0.0068	0.357
	14	1.9103	1.8610	0.0493	2.65
	15	1.9144	1.8863	0.0281	1.49
	$\bar{x}$			0.0380	2.04
	s			0.0209	1.13
Tank 36	11	1.8656	1.8902	-0.0246	1.30
	13	1.9210	1.8830	0.0380	2.02
	14	1.8753	1.8856	-0.0103	0.546
	15	1.8594	1.8718	-0.0124	0.662
	16	1.9059	1.8880	0.0179	0.948
	$\bar{x}$			0.00172	1.10
	s			0.0256	0.593

Replaced 17



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Performances of this work observed by: Disclosed to and understood by me:

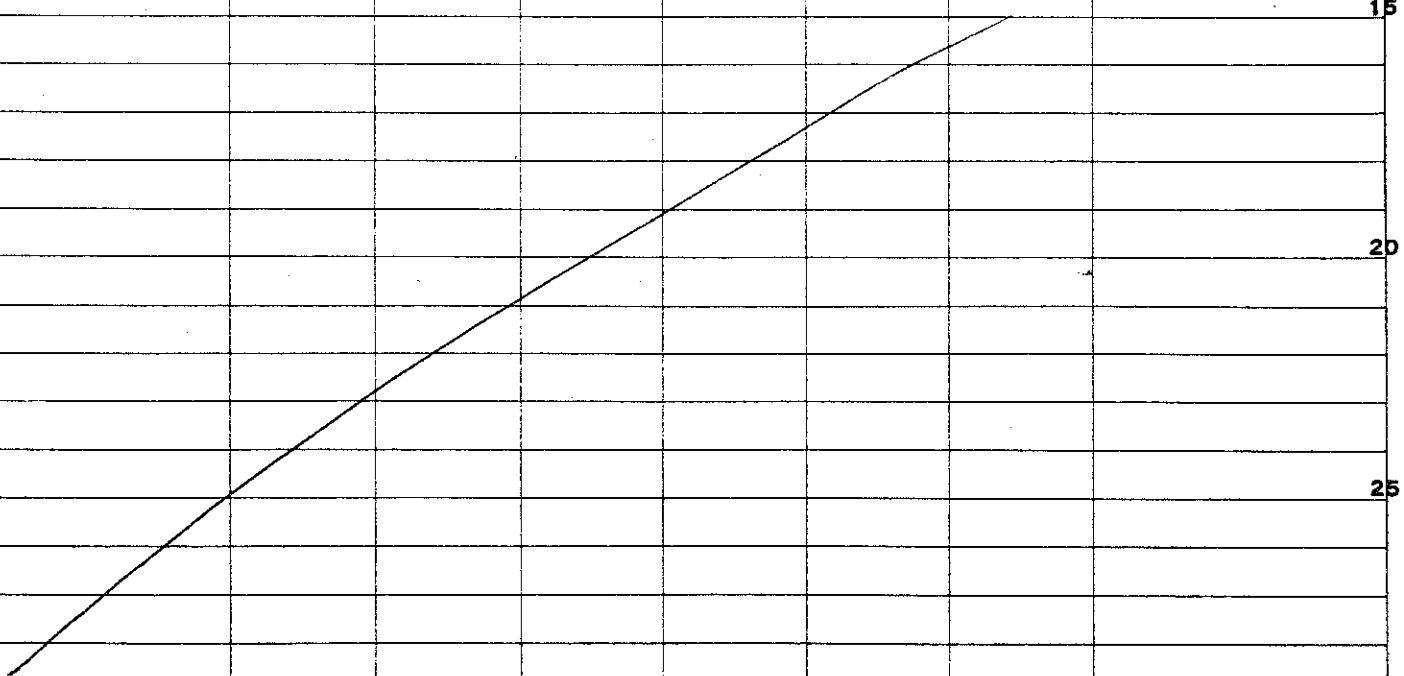
Date: Date:

Date: Date:

Work Performed by: R Huggins Project No. N0751-2413 Date of Work: 2/19/85

Title or Purpose: Sorption properties - Tank 37-90 day Continued from: —

		Sample wgt g	Initial wgt g	Weight change g	% change %
TANK 37	11	2.0030	1.9414	0.0616	3.17
	12	1.9067	1.8572	0.0495	2.67
	13	1.9137	1.8553	0.0584	3.15
	14	1.9560	1.8959	0.0601	3.17
	15	1.9464	1.8895	0.0569	3.01
	$\bar{x}$			0.0573	3.03
	s			0.00470	0.214



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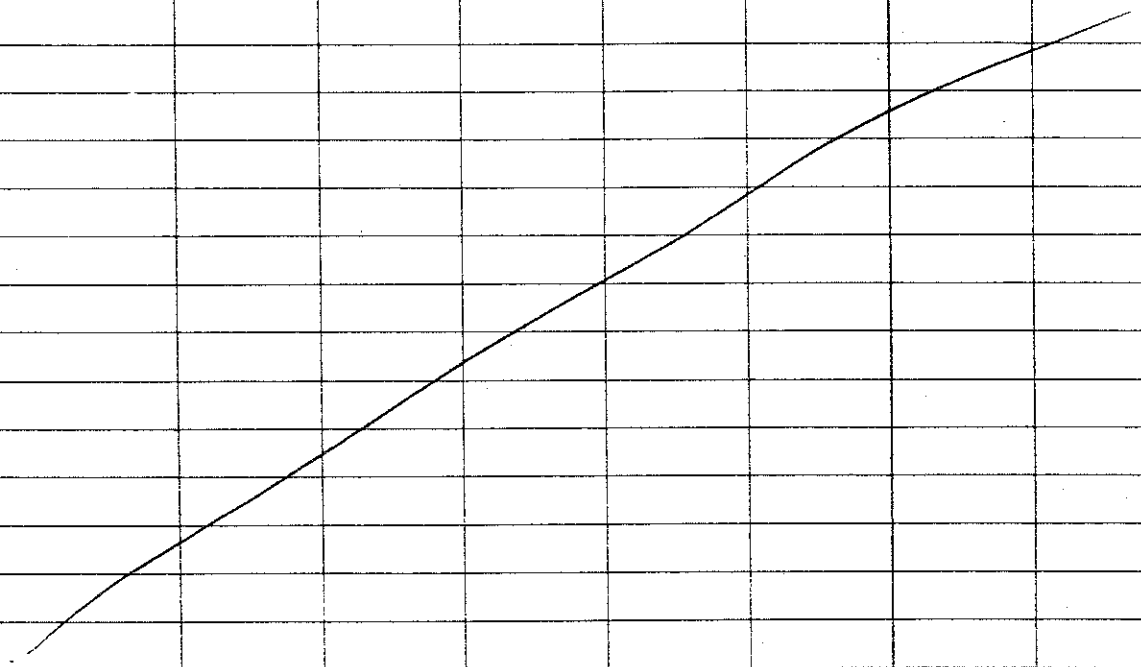
Performances of this work observed by:	Disclosed to and understood by me:
Date:	Date:
Date:	Date:

Work Performed by: R Huggins Project No. N0751-2413 Date of Work: 2/7/85

Title or Purpose: Sorption properties - tank 38 - 90 days Continued from: —

		Sample wgt g	Initial wgt g	Weight change g	% change %
TANK 38	11	2.0210	1.9998	0.0212	1.06
	12	1.9603	1.9411	0.0192	0.989
	13	1.9169	1.8972	0.0197	1.04
	14	1.8764	1.8570	0.0194	1.04
	15	1.9635	1.9422	0.0213	1.10
	$\bar{x}$			0.0202	1.04
	s			0.00101	0.0401



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Performances of this work observed by:	Disclosed to and understood by me:
Date:	Date:
Date:	Date:

Work Performed by: R Huggins Project No. N0751-2404 Date of Work: 11/16/84

Title or Purpose: Sorption properties - 121 deg exp Continued from: —

		Sample wgt g	Initial wgt g	Weight change g	% change %
TANK 35	(16) 1	1.8667	1.8924	-0.0257	1.36
	(17) 2	1.8564	1.8391	0.0173	0.941
	(18) 3	1.9091	1.8289	0.0802	4.38
	(19) 4	1.9137	1.8913	0.0224	1.18
	(20) 5	1.8896	1.8362	0.0534	2.91
	(21) 6	1.8698	1.8462	0.0236	1.28
	(22) 7	1.8595	1.8453	0.0142	0.770
	(23) 8	1.8691	1.8441	0.0250	1.36
	(24) 9	1.8767	1.8743	0.0024	0.13
	(25) 10	1.9097	1.8397	0.0700	3.80
	(26) 11	1.8959	1.8526	0.0433	2.34
	(27) 12	1.9017	1.8452	0.0565	3.06
	(28) 13	1.8880	1.8393	0.0487	2.65
	(29) 14	1.8568	1.8599	-0.0031	0.17
	(30) 15	1.8825	1.8597	0.0228	1.23
	$\bar{x}$			0.0301	1.84
	s			0.0286	1.28

Entered by: R Huggins Date: 11/26/84 Continued to: 26

Performances of this work observed by: Disclosed to and understood by me:

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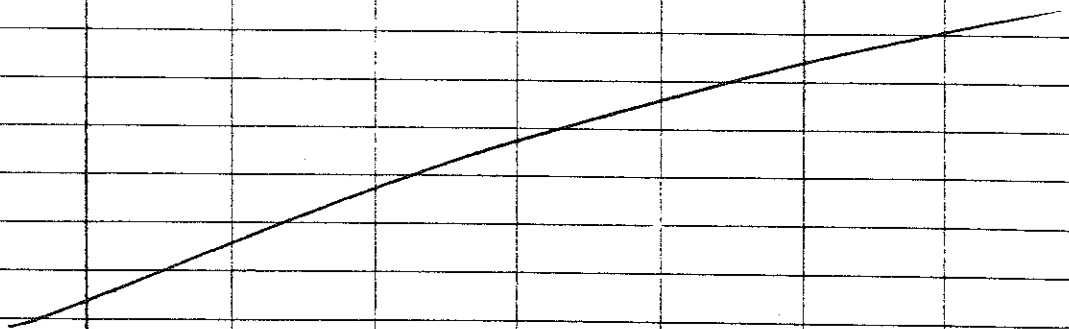
Date: Date:

Work Performed by: R Huggins Project No. N0751-2404 Date of Work: 11/16/84

Title or Purpose: Sorption properties - 121 day exp. Continued from:

		Sample wgt g	Initial wgt g	Weight change g	% change %
Tank 36	(1) 17	1.8538	1.8415	0.0123	0.668
	(2) 18	1.8434	1.8838	-0.0404	2.14
	(3) 19	1.9062	1.8855	0.0207	1.10
	(4) 20	1.8514	1.8603	-0.0089	0.48
	(5) 21	1.8619	1.8373	0.0246	1.34
	(6) 22	1.8614	1.8304	0.0310	1.69
	(7) 23	1.8600	1.8368	0.0232	1.26
	(8) 24	1.8894	1.8499	0.0395	2.14
	(9) 25	1.8578	1.8772	-0.0194	1.03
	(10) 26	1.8684	1.8769	-0.0085	0.45
	(11) 27	1.9016	1.8651	0.0365	1.96
	(12) 28	1.8543	1.8321	0.0222	1.21
	(13) 29	1.8750	1.8333	0.0417	2.28
	(14) 30	1.8738	1.8581	0.0157	0.845
	(15) 31	1.8531	1.8324	0.0207	1.13
	$\bar{X}$			0.0152	1.31
	S			0.0226	0.604



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Performances of this work observed by: Disclosed to and understood by me:

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Work Performed by: K Hugg Project No. N0751-2413 Date of Work: 3/21/85

Title or Purpose: Sorption properties - tank 37 - 120 day exp. Continued from: —

TANK 37	Sample wgt g	Initial wgt g	Weight change g	% change %	Neutral
16	1.9203	1.8514	0.0689	3.72	
17	1.9562	1.8843	0.0719	3.82	
18	1.9108	1.8494	0.0614	3.32	
19	1.9848	1.9164	0.0684	3.57	
20	1.9593	1.8948	0.0645	3.40	
21	1.9769	1.9073	0.0696	3.65	
22	1.9793	1.9099	0.0694	3.63	
23	1.9426	1.8832	0.0594	3.15	
24	1.9775	1.9276	0.0499	2.59	
25	1.9456	1.9035	0.0421	2.21	
26	1.8089	1.7685	0.0404	2.28	
27	1.9543	1.9135	0.0408	2.13	
28	1.9397	1.8902	0.0495	2.62	
29	1.9661	1.9132	0.0529	2.76	
30	2.0006	1.9458	0.0548	2.82	
$\bar{X}$			0.0576	3.04	
s			0.0112	0.591	

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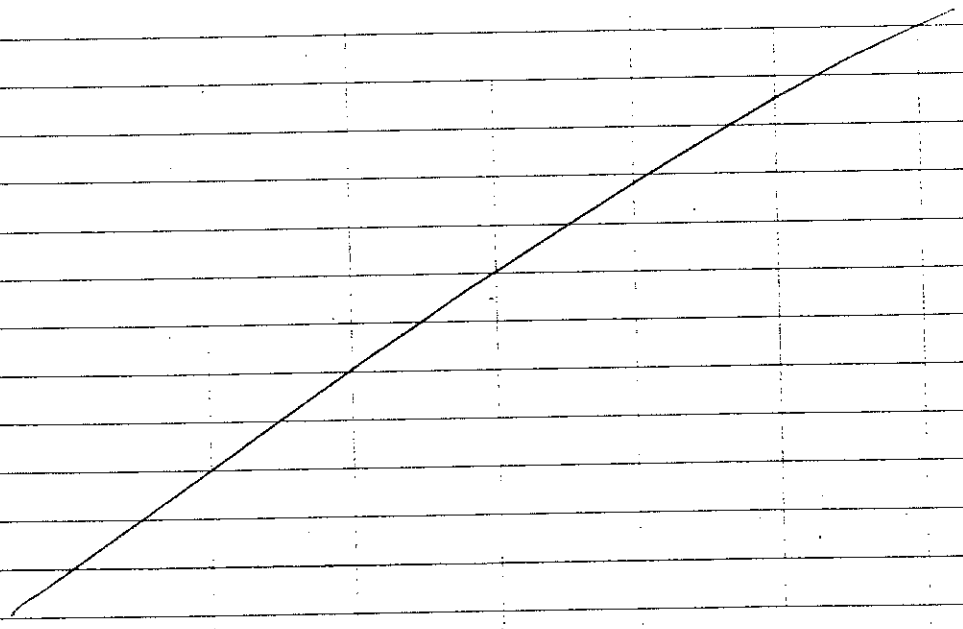
Performances of this work observed by:	Disclosed to and understood by me:
Date:	Date:
Date:	Date:

Work Performed by: R Huggins Project No. N0751-2413 Date of Work: 4/5/85

Title or Purpose: Sorption properties - tank 38 119 day exp Continued from: —

	Sample wgt g	Initial Weight wgt g	Weight change g	% change %
16	1.8954	1.8748	0.0206	1.10
17	1.9224	1.9013	0.0211	1.11
18	1.8706	1.8503	0.0203	1.10
19	1.8963	1.8758	0.0205	1.09
20	1.9138	1.8931	0.0207	1.09
21	1.9164	1.8951	0.0213	1.12
22	1.9517	1.9298	0.0219	1.13
$\bar{X}$			0.0209	1.10
s			0.0006	0.0151



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Performances of this work observed by:

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Disclosed to and understood by me:

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FINAL REPORT

on

ASSESSMENT OF WASTE SLUDGE STABILIZATION ALTERNATIVES

to

CHEMICAL WASTE MANAGEMENT, INC.
OAK BROOK, ILLINOIS

July 13, 1984
July 13, 1984

by

Bruce W. Vigon and Fred L. DeRoos

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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FINAL REPORT

on

ASSESSMENT OF WASTE SLUDGE STABILIZATION ALTERNATIVES

to

CHEMICAL WASTE MANAGEMENT, INC.
OAK BROOK, ILLINOIS

by

Bruce W. Vigon and Fred L. DeRoos

July 13, 1984

BATTELLE
Columbus Laboratories

OBJECTIVES

The hazardous waste facility at Vickery, Ohio, owned by Chemical Waste Management, Inc. contains several large lagoons that have been used for the temporary storage of waste oil and other materials. These materials range from liquids to semi-solids and have, over the years, caused a layer of contaminated sludge to build up on the pond bottom.

Chemical Waste Management, Inc., plans to close one of these ponds permanently and is demonstrating the effectiveness of the pond closure program in attenuating these contaminants to levels below regulatory concern. As a part of the engineering program, Chemical Waste Management, Inc., has developed recipes for six different sludge stabilization systems which may prove effective in controlling leachate production and quality.

The general objective of this research was to provide information which could be used in the selection of a sludge fixation system for the site.

The specific objectives of this research were threefold:

(1) Characterize the unstabilized sludge and raw solidification matrix materials using state-of-the-art chemical analytical

techniques to establish reference baseline conditions for subsequent stabilization methodology evaluation.

(2) Prepare test specimens for leaching experiments that are consistent with current standard Extraction Procedure (EP) toxicity methodology as described in the Federal Register, May 19, 1980, and amplified by EPA Publication SW-846 "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" (1982), and

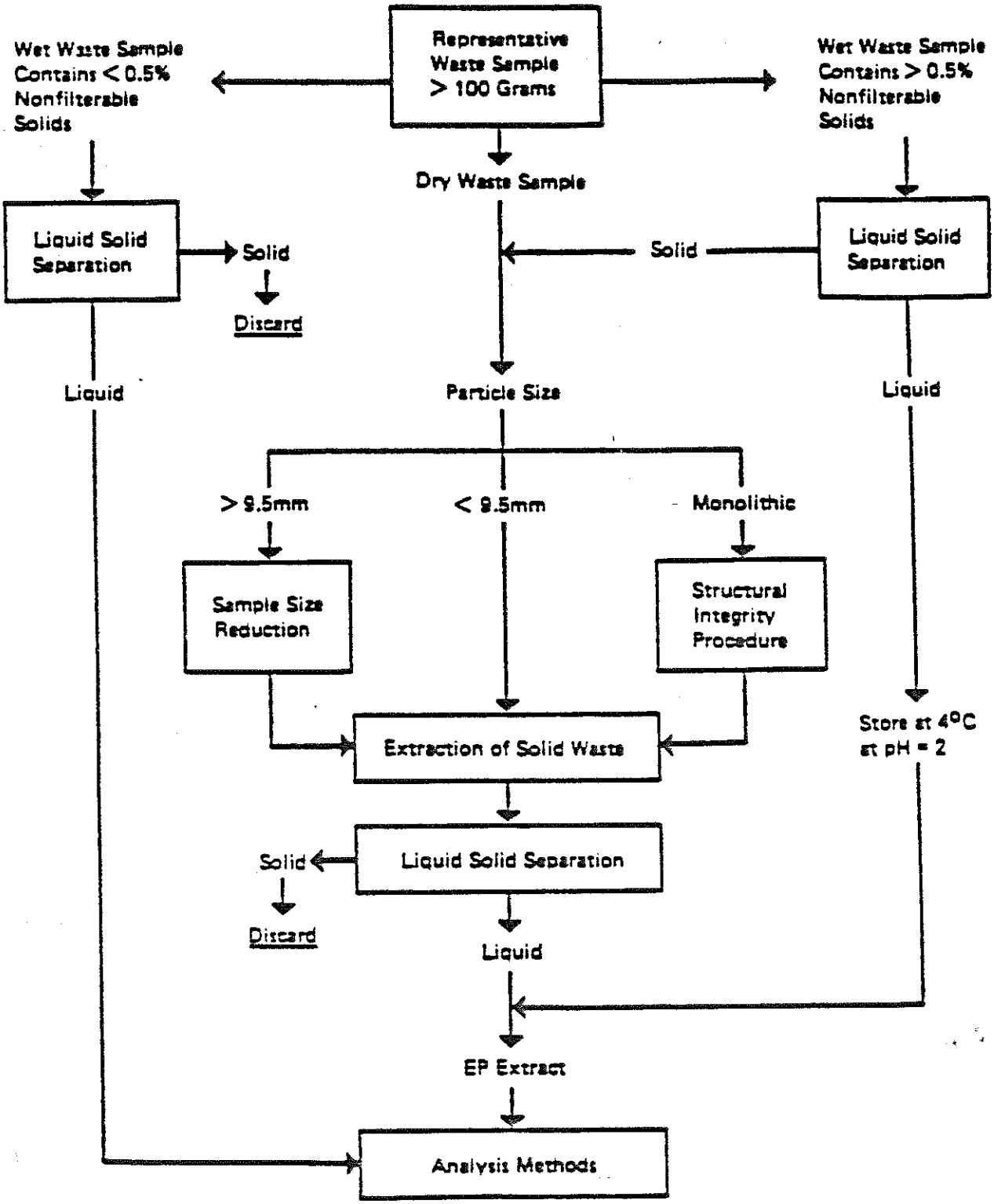
(3) Analyze the effectiveness of the six stabilization alternatives in two ways. First, compare the relative attenuation of each alternative to each other and to the unfixed reference baseline. Second, where reasonable contaminant specific water quality concentrations can be established by their EP toxic levels or a 30X multiplier of the ambient water quality criteria, compare the leachate concentrations to these target values.

RESULTS

This research program was divided into three phases--unfixed sludge and raw fixation materials characterization, fixed sludge leachate generation and comparison of fixed versus unfixed sludge leachate.

Phase I - Unfixed Sludge and Raw Fixation Materials Characterization

Samples of unfixed waste pond sludge and five fixation system components--kiln dust, beet tailings, fly ash, site clay and sulfate sludge--were subjected to extraction and analysis. Three samples of sludge and the raw fixation materials were processed through the EP leaching procedure as shown in Figure 1. Details of the EP protocol are described in Appendix A. A third sludge sample was analyzed by exhaustive digestion/extraction to determine the total contaminant content. In this way an estimate could be made of the presence and availability of a contaminant.


Representative Waste Sample > 100 Grams
Wet Waste Sample Contains < 0.5% Nonfilterable Solids
Wet Waste Sample Contains > 0.5% Nonfilterable Solids
Dry Waste Sample
Liquid Solid Separation
Solid
Discard
Solid
Liquid Solid Separation
Liquid
Particle Size
Liquid
> 9.5mm
< 9.5mm
Monolithic
Sample Size Reduction
Structural Integrity Procedure
Store at 4°C at pH = 2
Extraction of Solid Waste
Solid
Liquid Solid Separation
Discard
Liquid
EP Extract
Analysis Methods

Leachate or extract was analyzed for the following classes of contaminants using approved EPA protocols as indicated:

- Volatile organic priority pollutants (Method 624 Purge and Trap followed by GC/MS)
- 2,3,7,8 tetrachlorodibenzodioxin (GC/MS)
- Pesticides (Method 608 GC-ECD)
- Dichlorobenzidine (Method 605 HPLC-ED)
- Polychlorinated biphenyls (Method 608 GC)
- EP Toxic Metals (Method 8.8.3-ICAP/AA).

Detailed descriptions of the sample preparation and analysis protocols are contained in the appendices.

Analysis results for the raw fixation materials were examined for two purposes. First, high levels of contaminants in the raw fixation materials would be undesirable. Contributions of contamination from the raw fixation materials would place additional demands on the stabilization process. Second, if contaminants are not leached from either the fixative agents or the sludge, then Phase III analysis need not incorporate these parameters.

Volatile Organic Priority Pollutants

The Method 624 results from the analysis of the nine samples and three method blanks are shown in Table 1. The EP leachate analysis for the three sludge samples indicates the presence of detectable concentrations of several chlorinated aliphatic hydrocarbons. The concentrations of 1,2 dichloroethane and chloroform were significantly higher than the other analytes and would be good indicators of attenuation performance for this classof compounds.

Four aromatic compounds were also detected, with toluene and chlorobenzene present in concentrations above one milligram per liter. Stabilization performance for those recipes containing clay or other siliceous material has been closely watched because of reported shrinkage problems and poor material compatibility with these constituents.

Several organic species were detected in the EP extract that were not found in the methanol extract. In view of the much higher method

TABLE 1 - ANALYSIS OF RAW MATERIALS AND SLUDGE
VOLATILE PRIORITY POLLUTANTS-METHOD 624

SAMPLE

ANALYTE	RAW SLUDGE (a)	RAW SLUDGE (a)	RAW SLUDGE (b)	RAW SLUDGE (c)	FLY ASH	KILN DUST	VIRGIN CLAY	SULFATE SLUDGE	BEET TAILING	METHOD BLANK 1	METHOD BLANK 2	METHOD BLANK 3
	CONCENTRATION, ppb (except as noted)											
	(d)		(e)									
CHLOROMETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BROMOMETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
VINYL CHLORIDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CHLOROETHANE	ND	ND	ND	ND	ND(f)	ND	ND	ND	ND	ND	ND	ND
METHYLENE CHLORIDE	340	150	ND	6250	>220	>170	>100	4	>150	ND	ND	ND
ACETONE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
ACROLEIN	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TRICHLOROFLUOROMETHANE	ND	ND	ND	ND	ND	1	ND	ND	ND	ND	ND	ND
ACRYLONITRILE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-DICHLOROETHYLENE	27	37	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-DICHLOROETHANE	35	36	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-DICHLOROETHYLENE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CHLOROFORM	540	610	61	6300	1	1	ND	1	3	ND	ND	ND
1,2-DICHLOROETHANE	850	930	ND	39000	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-TRICHLOROETHANE	260	320	258	1438	3	3	2	4	2	1	ND	ND
CARBON TETRACHLORIDE	20	23	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BROMODICHLOROMETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-DICHLOROPROPANE	ND	9	ND	84	ND	ND	ND	ND	ND	ND	ND	ND
1,3-DICHLORO-1-PROPENE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TRICHLOROETHYLENE	78	97	86	240	ND	1	ND	ND	ND	ND	ND	ND
BENZENE	200	230	56	598	ND	1	1	ND	ND	ND	ND	ND
DIBROMOCHLOROMETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2-TRICHLOROETHANE	7	7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-CHLOROETHYL VINYL ETHER	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BROMOFORM	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-TETRACHLOROETHANE	12	ND	ND	28	ND	ND	ND	ND	ND	ND	ND	ND
TETRACHLOROETHYLENE	57	72	188	120	ND	1	ND	ND	ND	ND	ND	ND
TOLUENE	1400	1700	1180	1720	1	1	ND	1	1	1	ND	1
CHLOROBENZENE	1200	1500	1040	2700	ND	ND	ND	ND	ND	ND	ND	ND
ETHYLBENZENE	57	68	124	170	ND	ND	ND	ND	ND	ND	ND	ND

(a) EP Extract (100 gram sample).
(b) Methanol Extract.
(c) EP Extract of unfixed sludge for system VI, detection limit is 25 ppb.
(d) ND= Not Detected (<1 ppb), except as noted.
(d) Concentrations in this column are in mg/kg (ppm).
(e) Indicates gas chromatograph column/detector saturation.

detection limit (MDL) for the methanol extract (50 µg/g versus 5-10 µg/l) in the EP extract), these findings should not be construed as a lack of accuracy in the determination of total contaminant levels in the sludge.

Partition coefficients and extraction efficiencies were computed for the eight compounds where solid phase concentrations were detectable for the first sludge sample. Partition coefficients (concentration in solid phase divided by concentration in liquid EP extract phase) and extraction percentages confirmed that aqueous acetic acid is not a severe leaching agent for hydrophobic matrices and contaminants such as those examined in this study. Extraction efficiences averaged 1.2 percent and did not exceed 4.7 percent (chloroform).

With the exception of methylene chloride (suspected to be at least partially due to laboratory atmosphere contamination), only trace concentrations of this class of contaminants were leached from the raw fixation materials. These ingredients of the fixation system recipes should prove acceptable from the standpoint of not creating additional stabilization matrix problems.

Dioxin, Dichlorobenzidine, Pesticides and PCBs

This category of contaminants was less efficiently extracted than the Method 624 volatile organic compounds (Table 2). Dioxin was not detected at 3 ng/l (ppt) and PCBs were not detected at a level of 10 µg/l (ppb) in the EP leachate. Pesticides and herbicides were not found at detection levels ranging from 0.2 µg/l in the clean samples from the raw materials to 20 µg/l in the sludge leachate. Concentrations of 3,3'-dichlorobenzidine were below the level of detection of Method 605 using High Performance Liquid Chromatography coupled with an electrochemical detector. Detection levels were 1 µg/l in these samples.

The exhaustive analysis of the raw sludge, followed by high resolution mass spectrometry, of 2,3,7,8-TCDD indicated the presence of this isomer at 87 ng/g. Relative attenuation of TCDD by each of the four methods cannot be established with the EP protocol because the concentrations were below detectability. Although extracted interferences presented severe quantitation problems for the analysis of total PCB content, a similar

TABLE 2- ANALYSIS OF RAW MATERIALS AND SLUDGE
2,3,7,8-DIOXIN, DICHLOROBENZIDINE, PESTICIDES and PCBs

ANALYTE	SAMPLE: RAW SLUDGE (a)	RAW SLUDGE (a)	RAW SLUDGE (b)	RAW SLUDGE (c)	FLY ASH	KILN DUST	VIRGIN CLAY	SULFATE SLUDGE	BEET TAILINGS
	CONCENTRATION, ppb (except as noted)								
2,3,7,8 TETRACHLORODIBENZO-DIOXIN	<0.003	<0.002	87	<0.0001	---	---	---	---	---
3,3'DICHLOROBENZIDINE	<1	<1	<1	<1	---	---	<1	<1	<1
ENDRIN	<2	<2	<10 (d)	<2	<0.02	<0.02	<0.02	<0.02	<0.02
LINDANE	<2	<2	<10 (d)	<2	<0.02	<0.02	<0.02	<0.02	<0.02
METHOXYCHLOR	<10	<10	<50 (d)	<10	<0.10	<0.10	<0.10	<0.10	<0.10
TOXAPHENE	<20	<20	<100 (d)	<20	<0.20	<0.20	<0.20	<0.20	<0.20
2,4-D	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
2,4,5-TP (SILVEX)	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
PCBs(as Arochlor mixture)	<10	<10	<500 (d),(e)	<10	<0.10	<0.10	<0.10	<0.10	<0.10

(a) EP Extract (100 gram sample).
(b) Solvent Extract.
(c) EP Extract for unfixed sludge from system VI.
(d) Concentration in mg/kg (ppm).
(e) Based on observation of chromatograms, concentrations are probably in the 50-100 mg/kg range but confirmation is not possible due to interferences.

negative comment applies to the use of this contaminant group as an indicator of fixation potential. The exhaustive analysis for pesticides and herbicides likewise was unsuccessful in finding these contaminants at detection levels ranging from 10 to 100 mg/kg. Dichlorobenzene was not detected in the exhaustive solvent extract of the sludge. Samples of the kiln dust and fly ash were not analyzed for DCB because the high temperature environment in which they were formed would have destroyed any traces of DCB.

Metals

Four of the eight EP toxicity metals were detected in the EP leachate from first the raw sludge (Table 3). However, only lead was present above 100 parts per billion. As was observed for the EP extraction efficiencies for the Method 624 contaminants, most of the considerable metal content (especially chromium and lead) was unavailable given the leaching conditions of the experiment. Only selenium was below detection in the EP leachate from the second sludge with arsenic, chromium and lead found in excess of 1 part per million.

Of the raw fixation materials, the fly ash exhibited very high leachate concentrations of lead and moderately high concentrations of barium, chromium, and mercury. The remaining raw materials had detectable barium concentrations but EP toxic concentrations are well above the observed levels. The clay also leached (barely) detectable amounts of lead and a trace of mercury was found in the beet tailings.

Phase II Fixation System Sample Preparation and Leaching

This research activity was initiated for the first four systems on April 12, 1984. System V was mixed on May 18 followed by System VI on May 25. Samples of each of the six fixation alternative mixtures were prepared using the recipes shown in Table 4. Each of the ingredients was weighed out into a tared glass jar and mixed thoroughly with a Teflon spatula for approximately 15 minutes. Any lumps present in the raw materials were pulverised prior to mixing to ensure a reasonably homogeneous matrix. After the initial mixing

TABLE 3. ANALYSIS OF RAW MATERIALS AND SLUDGE
METALS

ANALYTE	SAMPLE: RAW SLUDGE (a)	RAW SLUDGE (a)	RAW SLUDGE (b)	RAW SLUDGE (c)	FLY ASH	KILN DUST	VIRGIN CLAY	SULFATE SLUDGE	BEET TAILINGS	METHOD BLANK
	CONCENTRATION, ppb (except as noted)									
ARSENIC	<100	<100	41 (d),(e)	5810	<100	<100	<100	<100	<100	<100
BARIUM	76	64	63 (d)	70	630	390	460	110	140	12
CADMIUM	12	9	9.1 (e)	90	<5	<5	<5	<5	<5	<5
CHROMIUM	58	48	330 (d)	10820	580	<10	<10	21	<10	<10
LEAD	550	560	380 (d)	2230	73300	<50	57	<50	<50	<50
MERCURY	<0.3	<0.3	5.6 (d)	0.3	6.8	<0.3	<0.3	<0.3	4.5	<0.3
SELENIUM	<100	<100	9.3 (d)	<100	<100	<100	<100	<100	<100	<100
SILVER	<10	<10	0.9 (d)	20	<10	<10	<10	<10	<10	<10

(a) EP Extract (100 gram sample).
(b) Acid Digestion Extract.
(c) EP Extract from unfixed sludge for system VI.
(d) Concentrations in mg/kg (ppm); value is mean of duplicate analyses.
(e) May be biased high due to aluminum interference.

TABLE 4. COMPOSITION OF THE SIX SLUDGE FIXATION ALTERNATIVES

System I - CONSISTED OF THE FOLLOWING:	
100 parts Sludge	550 grams
35 parts Kiln Dust	192.5 grams
40 parts Sugar Beet Tailings	200 grams
15 parts Steel Pickle Liquor	82.5 grams
System II - CONSISTED OF THE FOLLOWING:	
100 parts Sludge	500 grams
20 parts Kiln Dust	100 grams
60 parts Clean Site Clay	300 grams
System III - CONSISTED OF THE FOLLOWING:	
100 parts Sludge	500 grams
20 parts Kiln Dust	100 grams
30 parts Flyash	150 grams
30 parts Calcium Sulfate Sludge	150 grams
System IV - CONSISTED OF THE FOLLOWING:	
100 parts Sludge	700 grams
30 parts Kiln Dust	210 grams
20 parts Calcium Sulfate Sludge	140 grams
System V - CONSISTED OF THE FOLLOWING:	
100 parts Sludge	1000 grams
30 parts Kiln Dust	300 grams
20 parts Portland Cement	200 grams
System VI - CONSISTED OF THE FOLLOWING:	
100 parts Sludge	1000 grams
20 parts Kiln Dust	200 grams
20 parts Beet Tailings	200 grams
20 parts Portland Cement	200 grams

some agglomeration was observed due to moisture absorption and possibly reaction of the compounds.

Triplicate samples of each system were placed in Teflon tubes approximately 15 cm. in length and 2.5 cm. in diameter. The material was compressed by hand into the tubes to reduce the void space and no measurements of compaction density were made. A small amount of free liquid was squeezed out of the cores during this process and was returned to the sample container. The cores were allowed to cure at room temperature for about two weeks.

During the curing period, observations indicated that the material in the cores from the first four systems dried to a greater extent than the uncompacted material retained in the jars. Noticeable liquid was present in the bulk mixtures in the jars while none was observable in the cores. The cores and loose material for Systems V and VI were similar in appearance. Systems II and V exhibited the driest appearance probably due to their being composed entirely of dry additives to the sludge while the other systems contained liquid or paste-like components.

On April 25, the twelve cores from the first four systems were extruded from the tubes. On June 1 System V was extruded followed by System VI on June 8. All exhibited a dry appearance with the systems containing calcium sulfate having a yellow-white crust at both ends of the core. With the exception of Systems II and V, the material was plastic and moldable rather than friable in nature. This raised some questions regarding preparation of the samples for EP testing. Systems I, II, IV and VI were not pulverizable prior to seiving to achieve the required sample size reduction to below 9.5 mm. Because the addition of the leaching medium disperses the material, forcing the sample through the seive openings was not felt to compromise the extraction efficiency. The EP leaching conditions are summarized in Table 5.

Leachate from each sample was taken through the filtration step of the EP technique using Millipore filters in a pressure filtration apparatus. Aliquots were then subjected to further processing as described in the appendices.

TABLE 5. EP EXTRACTION CONDITIONS

Sample I.D.	Mass of Sample, grams	Volume of D.I. water, ml.	Amt. of(a) leachant, ml.	Initial pH	Final pH	Final Volume after leaching, ml.
System 1, Replicate 1	65	1175	125	9.24	5.15	1200
System 1, Replicate 2	70	1275	125	9.20	5.09	1200
System 1, Replicate 3	70	1275	125	9.18	5.18	1200
System 2, Replicate 1	80	1475	125	9.92	5.14	1400
System 2, Replicate 2	70	1275	125	9.95	5.11	1300
System 2, Replicate 3	80	1475	125	9.96	5.21	1400
System 3, Replicate 1	75	1250	250	11.52	4.91	1400
System 3, Replicate 2	70	1150	250	11.55	4.93	1300
System 3, Replicate 3	75	1250	250	11.57	4.97	1400
System 4, Replicate 1	75	1300	200	10.56	5.17	1450
System 4, Replicate 2	80	1400	200	10.49	5.20	1500
em 4, Replicate 3	85	1500	200	10.16	5.16	1600
System 5, Replicate 1	85	1360	340	10.27	5.10	1700
System 5, Replicate 2	95	1550	350	10.34	5.17	1900
System 5, Replicate 3	100	1650	350	10.32	5.15	2000
System 6, Replicate 1	86	1376	340	10.50	4.89	1720
System 6, Replicate 2	81	1296	340	10.47	4.89	1650
System 6, Replicate 3	79	1269	340	10.37	4.88	1609
Blank 1	--	1350	150	5.38	4.25	1450
Blank 2	--	1200	300	6.21	2.70	1500
Blank 3	--	1200	300	4.50	2.90	1500

(a) Leachant for all systems was 0.5N acetic acid.

Phase III - Comparison of Fixed Versus Unfixed Sludges

The EP leachate characteristics for each of the six alternative fixation systems were compared to the EP leachate quality for the unfixed sludge determined during Phase I. In addition, the relative performance of each system in attenuating specific organic and inorganic constituents known to be leached from the unfixed sludge was assessed.

Volatile Organic Priority Pollutants

The results of the triplicate analysis of the fixed materials for Method 624 priority pollutants are shown in Table 6. Those analytes detected in the Phase I leachate generally were above detection in the leachate from the fixed material. The effect of mixture preparation, volatilization, or differential solute retention is apparent in the greater variability among replicates of the fixed material than was observed with the unfixed sludge samples.

Despite this variability, there are some distinct trends apparent in the behavior of each system relative to one another and in comparison with the unfixed material. The data on attenuation performance displayed in Table 7 compare the average concentrations of those Method 624 contaminants found in EP leachate from the fixed materials to the concentrations that are calculated to occur on the basis that each component of the fixation recipe contributes proportionately to the measured leachate concentration. The proportionate contribution from each component was determined by multiplying each of the Phase I sludge and raw materials leachate concentrations by the weight fraction of the individual components and summing to obtain an estimate of the expected composite leachate. This approach takes into account the additive contaminant contribution from each component where the concentrations are greater than those in the unfixed sludge leachate or the diluting effect in the event that the concentrations in the additives are lower. The fact that the mixture comprises a different proportion of sludge in each system is also accounted for.

The measured concentrations of contaminants in the leachate from Systems I and III were consistently lower than those from System II and

TABLE 6. EP LEACHATE COMPARISON, UNFIXED VERSUS FIXED SLUDGE
VOLATILE PRIORITY POLLUTANTS-METHOD 624

ANALYTE	RAW (a) SLUDGE REPLICATE 1	RAW (a) SLUDGE REPLICATE 2	RAW (b) SLUDGE REPLICATE 1	METHOD BLANK	SYSTEM 1 REPLICATE 1	SYSTEM 1 REPLICATE 2	SYSTEM 1 REPLICATE 3	SYSTEM 1 AVERAGE	SYSTEM 2 REPLICATE 1	SYSTEM 2 REPLICATE 2	SYSTEM 2 REPLICATE 3	SYSTEM 2 AVERAGE	SYSTEM 3 REPLICATE 1	SYSTEM 3 REPLICATE 2	SYSTEM 3 REPLICATE 3	SYSTEM 3 AVERAGE
		(d)			CONCENTRATION, ppb(c)											
CHLOROMETHANE	ND	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
BROMOMETHANE	ND	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
VINYL CHLORIDE	ND	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
CHLOROETHANE	ND	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
METHYLENE CHLORIDE	340	150	6250	33	35	20	20	25	108	41	20	56	29	23	30	27
ACETONE	ND	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
ACROLEIN	ND	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
TRICHLOROFLUOROMETHANE	ND	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
ACRYLONITRILE	ND	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
1,1-DICHLOROETHYLENE	27	37	ND	ND	20	ND	ND	<7	151	ND	ND	<50	10	10	ND	<7
1,1-DICHLOROETHANE	35	36	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
1,2-DICHLOROETHYLENE	ND	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
CHLOROFORM	540	610	6300	10	15	10	13	13	47	130	12	63	32	14	48	31
1,2-DICHLOROETHANE	850	930	39000	ND	15	7	12	11	38	190	ND	76	40	20	68	43
1,1,1-TRICHLOROETHANE	260	320	1438	ND	6	6	9	7	122	143	8	91	30	9	60	33
CARBON TETRACHLORIDE	20	23	ND	ND	ND	ND	ND	<1	ND	8	ND	<3	ND	ND	ND	<1
BROMODICHLOROMETHANE	ND	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
1,2-DICHLOROPROPANE	ND	9	84	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
1,3-DICHLORO-1-PROPENE	ND	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
TRICHLOROETHYLENE	78	97	240	ND	10	ND	7	<6	18	48	ND	<22	18	11	25	18
BENZENE	200	230	598	10	27	15	15	19	35	71	14	40	28	16	33	26
DIBROMOCHLOROMETHANE	ND	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
1,1,2-TRICHLOROETHANE	7	8	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
2-CHLOROETHYL VINYL ETHER	ND	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
BROMOFORM	ND	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	<1	ND	ND	ND	<1
1,1,2,2-TETRACHLOROETHANE	12	ND	28	ND	ND	ND	ND	<1	12	ND	ND	<5	ND	ND	ND	<1
TETRACHLOROETHYLENE	57	72	120	ND	38	10	23	24	58	67	15	47	35	31	47	38
TOLUENE	1400	1700	1720	ND	400	107	235	247	740	1060	119	640	500	360	615	492
CHLOROBENZENE	1200	1500	2700	ND	980	229	440	550	1300	1190	290	927	880	680	845	802
ETHYLBENZENE	57	68	170	ND	103	19	29	50	130	55	22	69	39	36	41	39

a) Unfixed sludge sample for systems I to V.
b) Unfixed sludge sample for system VI, detection limit is 25 ppb.
(c) All concentrations are in micrograms/ liter (ppb) of EP leachate.
(d) ND = not detected (<1 ppb), except as noted.

TABLE 6. EP LEACHATE COMPARISON, UNFIXED VERSUS FIXED SLUDGE (continued)
VOLATILE PRIORITY POLLUTANTS-METHOD 624

ANALYTE	RAW (a) SLUDGE REPLICATE 1	RAW (a) SLUDGE REPLICATE 2	METHOD BLANK	SYSTEM 4 REPLICATE 1	SYSTEM 4 REPLICATE 2	SYSTEM 4 REPLICATE 3	SYSTEM 4 AVERAGE	METHOD BLANK	SYSTEM 5 REPLICATE 1	SYSTEM 5 REPLICATE 2	SYSTEM 5 REPLICATE 3	SYSTEM 5 AVERAGE	RAW (b) SLUDGE REPLICATE 1	METHOD BLANK	SYSTEM 6 REPLICATE 1	SYSTEM 6 REPLICATE 2	SYSTEM 6 REPLICATE 3	SYSTEM 6 AVERAGE
	CONCENTRATION, ppb (c)																	
CHLOROMETHANE	ND (d)	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
BROMOMETHANE	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
VINYL CHLORIDE	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
CHLOROETHANE (e)	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
METHYLENE CHLORIDE	340	150	33	27	59	26	37	99	305	189	186	227	6250	170	450	550	550	517
ACETONE	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
ACROLEIN	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
TRICHLOROFLUOROMETHANE	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
ACRYLONITRILE	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
1,1-DICHLOROETHYLENE	27	37	ND	30	39	16	28	ND	16	16	16	16	ND	ND	18	18	21	19
1,1-DICHLOROETHANE	35	36	ND	ND	23	ND	<8	ND	13	15	14	14	ND	ND	6	ND	8	<5
1,2-DICHLOROETHYLENE	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
CHLOROFORM	540	610	10	108	255	79	147	ND	447	428	450	442	6300	ND	1000	1300	1400	1381
1,2-DICHLOROETHANE	850	930	ND	160	366	134	220	ND	1529	1368	1400	1432	39000	ND	4400	5700	6200	5433
1,1,1-TRICHLOROETHANE	260	320	ND	115	269	75	153	1	224	232	250	235	1438	1	340	400	390	377
CARBON TETRACHLORIDE	20	23	ND	34	10	ND	15	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
BROMODICHLOROMETHANE	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
1,2-DICHLOROPROPANE	ND	9	ND	ND	5	ND	<2	ND	13	12	11	12	84	ND	36	43	45	41
1,3-DICHLORO-1-PROPENE	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
TRICHLOROETHYLENE	78	97	ND	49	76	33	53	ND	73	76	76	75	240	ND	89	100	120	103
BENZENE	200	230	10	67	121	50	79	1	141	147	150	146	598	2	190	230	230	217
DIBROMOCHLOROMETHANE	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
1,1,2-TRICHLOROETHANE	7	8	ND	ND	ND	ND	<1	ND	5	7	6	6	ND	ND	7	11	10	9
2-CHLOROETHYL VINYL ETHER	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
BROMOFORM	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1
1,1,2,2-TETRACHLOROETHANE	12	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	<1	28	ND	ND	ND	ND	<1
TETRACHLOROETHYLENE	57	72	ND	58	83	45	62	ND	67	63	65	65	120	ND	81	81	99	87
TOLUENE	1400	1700	ND	880	1390	740	1003	2	1765	1684	1700	1716	1720	2	1000	1100	1200	1100
CHLOROBENZENE	1200	1500	ND	1090	1390	970	1150	ND	1882	1895	1800	1859	2700	ND	1300	1300	1600	1433
ETHYLBENZENE	57	68	ND	53	58	51	54	ND	92	80	85	86	170	ND	110	110	130	117

(a) Unfixed sludge sample for Systems I to V.
(b) Unfixed sludge for System VI, detection limit is 25 ppb.
(c) All concentrations are in micrograms/ liter (ppb) of EP leachate.
(d) ND = not detected (<1 ppb), except as noted.
(e) Concentrations for systems V and VI have been corrected for the method blank.

TABLE 7. ATTENUATION PERFORMANCE OF FIXATION SYSTEMS
VOLATILE PRIORITY POLLUTANTS

ANALYTE	AVERAGE LEACHATE CONCENTRATIONS, ppb												AVERAGE ATTENUATION, PERCENT (a)					
	MEASURED						PREDICTED (b)											
	SYSTEM TEST EM 1	SYSTEM TEST EM 2	SYSTEM TEST EM 3	SYSTEM TEST EM 4	SYSTEM TEST EM 5	SYSTEM TEST EM 6	SYSTEM TEST EM 1	SYSTEM TEST EM 2	SYSTEM TEST EM 3	SYSTEM TEST EM 4	SYSTEM TEST EM 5	SYSTEM TEST EM 6	SYSTEM TEST EM 1	SYSTEM TEST EM 2	SYSTEM TEST EM 3	SYSTEM TEST EM 4	SYSTEM TEST EM 5	SYSTEM TEST EM 6
METHYLENE CHLORIDE	25	56	27	37	227	517	>192	>188	>192	>198	>198	>3.9(d)	>87	>70	>86	>81	0	>87 (c)
1,1-DICHLOROETHYLENE	<7	<50	<7	28	16	19	22	18	18	24	21	<16	>58	0	>60	0	24	--
1,1-DICHLOROETHANE	<1	<1	<1	<8	14	<5	19	20	20	24	24	<16	>95	>94	>94	>65	42	--
CHLOROFORM	13	63	31	147	442	1381	303	310	310	383	410	3.94(d)	96	80	90	62	0	65
1,2-DICHLOROETHANE	11	76	43	220	1432	5433	468	494	494	592	596	24.4(d)	98	85	91	63	0	78
1,1,1-TRICHLOROETHANE	7	91	33	153	235	377	153	161	161	193	195	899	95	43	80	21	0	58
CARBON TETRACHLORIDE	<1	<3	<1	15	<1	<1	12	13	13	15	15	<16	>91	>76	>92	0	>92	--
1,2-DICHLOROPROPANE	<1	<1	<1	<2	12	41	<3	<3	<3	<4	<3	53	--	--	--	--	--	22
TRICHLOROETHYLENE	<6	<22	18	53	75	103	46	49	49	59	58	150	>87	>56	64	9	0	31
BENZENE	19	40	26	79	146	217	113	120	120	144	144	374	83	67	78	45	0	42
1,1,2-TRICHLOROETHANE	<1	<1	<1	<1	6	9	<4	<4	<4	<5	<5	<16	--	--	--	--	--	--
1,1,2,2-TETRACHLOROETHANE	<1	<5	<1	<1	<1	<1	<4	<4	<4	<4	<5	18	--	--	--	--	--	>94
TETRACHLOROETHYLENE	24	47	38	62	65	87	34	36	36	43	44	75	29	0	0	0	0	0
TOLUENE	247	640	492	1003	1716	1100	816	862	862	1033	1039	1075	70	35	43	3	0	0
CHLOROBENZENE	550	927	802	1150	1859	1433	710	750	750	900	905	1688	29	0	0	0	0	15
ETHYLBENZENE	50	69	39	54	86	117	33	36	36	42	42	106	0	0	0	0	0	0

(a) Computed for all analytes detected in the leachate from the unfixed sludge.
(b) Calculated on the basis that each component contributes proportionately to the combined EP leachate. For example, chloroform was found at 540 and 610 ppb in the leachate from the unfixed sludge. Since System I comprises 100/190 weight fraction sludge, the predicted proportional contribution of chloroform from the sludge is (.526)(575)=302 ppb. The remaining ingredients used in System I are predicted to contribute 0.8 ppb for a total concentration of 303 ppb.
(c) Slight differences between percentages given and those obtainable from the data shown are due to rounding.
(d) Concentrations are in mg/l (ppm).

markedly lower than in the leachate from Systems IV and V. This finding is reasonable in view of the fact that System I components include sugar beet tailings as an organic phase capable of attenuating organic compounds as well as kiln dust whose large specific surface area should favor organic compound adsorption. System III, while not having an organic component, does have considerable adsorptive surface which may help explain its relatively good performance. The site clay in System II does not appear to be as effective in organic compound retention as are the components of System I or III. Clays having a 1:1 layer structure with no capability to hold molecules in the interlayer spaces generally show little affinity for organic compounds. Some 2:1 and 2:2 layer clays have been found to be incompatible with leachate containing aromatic organic compounds due to shrinkage and cracking. This effect, particularly for aromatics, has been noted in the literature.

System IV differed from System II principally in the omission of the fly ash. Sulfate sludge and kiln dust alone do not appear effective in controlling the mobility of these organics. Systems V and VI contained Portland Cement to assist in the solidification of the sludge in the fixation matrix. However, the oily nature of this sludge apparently interferes with the ability of the cement to undergo the pozzolanic reaction necessary to form a solid mass. Judging from both the appearance of the material, which was predominantly crumbly agglomerates ranging from sand size to about 20 cm. diameter, and the chemical analysis, the addition of cement provides neither structural strength nor adsorptive/absorptive capacity.

System VI contained both an organic constituent in the form of beet tailings and cementitious material. Due to the fact that all of the initial batch of sludge was exhausted in the preparation of the first five systems, System VI was made up with a new sludge obtained as a composite of material from Ponds 4 and 5. As is evident from the analysis of the EP leachate from the unfixed sludge, the levels of contamination in this second system are considerably greater than those measured for the first sludge sample. For this reason it is difficult to draw any firm conclusions regarding the performance of System VI relative to the other systems. Considering the concentrations involved, the observed performance of System VI is to be expected and is really not that poor based on the attenuation percentages.

The difficulty in the comparison of this system relative to the others lies in determining the hypothetical performance of this system at lower contamination levels. If the concentrations of contaminants in the solid phase were known for the second sludge sample, it may be possible to compute a partition coefficient for comparison with those obtained for the first sludge. This would answer the question of whether the systems are behaving as if they were different points on the same isotherm or were on several different isotherms. Therefore, while the performance of System VI can be evaluated directly, any comparisons to the other systems must remain speculative. Due to the variability of these samples, the quantitative differences observed in all six systems may not be statistically significant but the qualitative trends are chemically justifiable.

In general, the more toxic components of the leachate were retained more effectively than the less toxic constituents. In comparison with the ambient water quality criterion* multiplied by the 30X factor to account for dispersion in groundwater, concentrations of 1,1,1-trichloroethane, toluene, chlorobenzene, trichloroethylene and ethylbenzene in leachate from the first five systems are well below those corresponding to a 10^{-6} risk level.

The remaining contaminants, which were detected and for which water quality criteria are available, include 1,1-dichloroethylene, chloroform, 1,2-dichloroethane, carbon tetrachloride, benzene, 1,1,2 trichloroethane, 1,1,2,2-tetrachloroethane and tetrachloroethylene.

Risk levels above 1×10^{-5} are computed for chloroform (7.5×10^{-5}) and 1,2 dichloroethane (5.1×10^{-5}) in leachate from System V. Chloroform in leachate from Systems IV (2.5×10^{-5}) and II (1.1×10^{-5}) also exceeds this level. Risk levels for the other contaminants are in the 10^{-6} to 10^{-5} range. For the superior fixation alternative among the first five recipes (System I), the criterion risk levels for these two contaminants are 2.1×10^{-6} and 4.0×10^{-7}. These risk levels represent more than one and two orders of magnitude reduction, respectively.

Because of the greater initial contaminant concentrations, System VI exhibits the highest absolute risk levels, greater than 1×10^{-6}, for five of the contaminants as follows:

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* Federal Register, November 28, 1980.

Contaminant	Risk Level
Chloroform	2.3×10^{-4}
1,2-dichloroethane	1.9×10^{-4}
benzene	1.1×10^{-5}
tetrachlorethylene	3.6×10^{-6}
trichloroethylene	1.3×10^{-6}

Risk levels for 1,1,1 trichloroethane, chlorobenzene, toluene, and ethylbenzene are all below 1×10^{-7}.

In summary, based on both relative and absolute measures of the attenuation of volatile priority pollutants, System I appears preferable. System III provides nearly as good a performance level in this respect.

Dioxin, Dichlorobenzidine, Pesticides and PCBs

Excellent detection levels were achieved for 2,3,7,8-tetrachlorodibenzodioxin in the 18 samples from the six systems. Consistent with the Phase I results discussion, TCDD, while present in the raw sludge sample matrix, was not leached to a detectable degree from the fixed materials. None of the extracts from any of the six systems showed TCDD in amounts greater than 3 parts per trillion of EP leachate and most were well below this level (Table 8).

None of the ten samples showed detectable concentrations of 3,3' dichlorobenzidine at a detection limit of 1 ppb.

Pesticides and herbicides for which EP toxic concentrations have been specified were not detected in the sludge or in any of the raw materials assayed during Phase I. Therefore, analysis for these materials would not have been informative for the fixed materials. Expected concentrations would be well below EP toxic levels based on the Phase I data and the proportional prediction approach discussed previously.

Polychlorinated biphenyls, like TCDD, were confirmed as present in the raw sludge matrix, although not satisfactorily quantifiable due to extreme hydrocarbon interference. Likewise, this class of contaminants was not extracted by the EP test as evidenced by the uniformly less than detectable concentrations (<10 ppb) in all 18 fixed sludge samples and in all three unfixed sludge samples.

TABLE 8. EP LEACHATE COMPARISON, FIXED VERSUS UNFIXED SLUDGE
DIOXIN, PCBs, AND DICHLOROBENZIDINE

SAMPLE	2,3,7,8-Tetrachloro-dibenzodioxin	3,3'-Dichloro-benzidine	PCBs (as Arochlor mixture)
		CONCENTRATION, ppb	
RAW SLUDGE I (a)			
Replicate 1	<0.003	<1	<10
Replicate 2	<0.002	<1	<10
Average	<0.003	<1	<10
SYSTEM 1			
Replicate 1	<0.0005	---	<10
Replicate 2	<0.0005	---	<10
Replicate 3	<0.0026	---(b)	<10
Average	<0.0012	<1	<10
SYSTEM 2			
Replicate 1	<0.0006	---	<10
Replicate 2	<0.0005	---	<10
Replicate 3	<0.0006	---(b)	<10
Average	<0.0006	<1	<10
SYSTEM 3			
Replicate 1	<0.0032	---	<10
Replicate 2	<0.0005	---	<10
Replicate 3	<0.0006	---(b)	<10
Average	<0.0014	<1	<10
SYSTEM 4			
Replicate 1	<0.0006	---	<10
Replicate 2	<0.0007	---	<10
Replicate 3	<0.0006	---(b)	<10
Average	<0.0007	<1	<10
SYSTEM 5			
Replicate 1	<0.0001	---	<10
Replicate 2	<0.0001	---	<10
Replicate 3	<0.0001	---(b)	<10
Average	<0.0001	<1	<10
RAW SLUDGE II (c)			
Replicate 1	<0.0001	<1	<10
SYSTEM 6			
Replicate 1	<0.0001	---	<10
Replicate 2	<0.0001	---	<10
Replicate 3	<0.0001	---(b)	<10
Average	<0.0001	<1	<10

(a) Raw sludge sample used for Systems I to V.
(b) Composite sample analysis.
(c) Raw sludge sample used for System VI.

Metals

Concentrations of EP metals in the leachates from the fixed sludges were less variable than was the case for the volatile organic contaminants. Replicate variation ranged from less than 10 percent to 250 percent and was typically 25 percent as summarized in Table 9.

Given the high EP lead concentrations in the fly ash, it was not surprising that the lead concentrations in System III were far above the lead levels in any of the other three systems. More unexpected was the observation of relatively high levels of arsenic in Systems IV, V and VI. The addition of the fly ash component in System III apparently contributes significantly to the adsorption or precipitation of arsenic. Control of arsenic leaching is partly due to oxidation-reduction as well as pH conditions. Typical scrubber sludges are known to be mixtures of calcium sulfate and calcium sulfite unless forced oxidation is employed. Redox and pH conditions following mixing to form System IV may have dramatically enhanced the arsenic solubility to produce the observed results. The Portland Cement may also be responsible for some of the arsenic found in leachate from Systems V and VI.

A comparison of the performance of the six systems for attenuation of metals is shown as Table 10. The observed results indicate not only the elevated arsenic and lead concentrations mentioned above but also the relatively high concentrations of cadmium in System III and of chromium in Systems IV and VI. The percentage attenuation of most constituents could not be computed because both the predicted and measured average concentrations contained at least one analysis below the detection limit.

Measured concentrations of EP metals were compared to the established EP toxic levels. Lead concentrations in System III reached 31 percent of the toxic level and arsenic concentrations in System VI were measured at 17 percent of the allowable concentration. All other metal concentrations were less than 10 percent of the EP toxic level. To statistically test whether metal concentrations were below the EP toxic level, a one-tail t-test was applied to the data for each metal and each system. The hypothesis tested was whether the mean leachate concentrations were below the EP toxic level ($\mu < \mu o$) at the 5% significance level. The results of this exercise confirmed that indeed all metal concentrations were below the EP limits.

TABLE 9. EP LEACHATE COMPARISON, UNF[illegible]D VERSUS FIXED SLUDGE
METALS

ANALYTE	RAW (a) SLUDGE REPLICATE 1	RAW (a) SLUDGE REPLICATE 2	SYSTEM 1 REPLICATE 1	SYSTEM 1 REPLICATE 2	SYSTEM 1 REPLICATE 3	SYSTEM 1 AVERAGE	SYSTEM 2 REPLICATE 1	SYSTEM 2 REPLICATE 2	SYSTEM 2 REPLICATE 3	SYSTEM 2 AVERAGE	SYSTEM 3 REPLICATE 1	SYSTEM 3 REPLICATE 2	SYSTEM 3 REPLICATE 3	SYSTEM 3 AVERAGE
							CONCENTRATION, ppb (b)							
ARSENIC	<100	<100	<100	120	<107	<100	<100	<100	<100	<100	<100	<100	<100	<100
BARIUM	76	64	130	110	120	120	160	200	200	187	240	300	230	257
CADMIUM	12	9	<5	<5	<5	<5	<5	7	6	<6	80	80	70	77
CHROMIUM	58	48	200	160	180	180	40	140	90	90	70	130	100	100
LEAD	550	560	<50	<50	<50	<50	<50	140	70	87	1060	2600	1050	1570
MERCURY	<0.3	<0.3	0.8	<0.3	<0.3	<0.5	<0.3	<0.3	<0.3	<0.3	5.6	<0.3	<0.3	<2.1
SELENIUM	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
SILVER	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

(a) EP Extract from unfixed sludge for systems I to V.
(b) Concentrations are in micrograms/ liter (ppb) of EP leachate.
(c) EP Extract from unfixed sludge for system VI.

TABLE 9. EP LEACHATE COMPARISON, UNFIXED FILTER CAKE (continued)
TOTALS

ANALYTE	RAW (a) SLUDGE REPLICATE 1	RAW (a) SLUDGE REPLICATE 2	SYSTEM 4 REPLICATE 1	SYSTEM 4 REPLICATE 2	SYSTEM 4 REPLICATE 3	SYSTEM 4 AVERAGE	SYSTEM 5 REPLICATE 1	SYSTEM 5 REPLICATE 2	SYSTEM 5 REPLICATE 3	SYSTEM 5 AVERAGE	RAW (b) SLUDGE REPLICATE 1	SYSTEM 6 REPLICATE 1	SYSTEM 6 REPLICATE 2	SYSTEM 6 REPLICATE 3	SYSTEM 6 AVERAGE
	CONCENTRATION, ppb (c)														
ARSENIC	<100	<100	190	170	230	197	330 (d)	360 (d)	400 (d)	363	5810	780 (d)	840 (d)	900 (d)	840
BARIUM	76	64	190	220	200	203	390	350	380	373	70	330	370	390	363
CADMIUM	12	9	7	<5	6	<6	<5 (d)	<5 (d)	60 (d)	<23	90	20	20	20	20
CHROMIUM	58	48	380	150	310	280	100	100	100	100	10820	190	220	260	223
LEAD	550	560	160	80	120	120	120	150	230	167	2230	<50	<50	80	<60
MERCURY	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	0.3	<0.3	<0.3	<0.3	<0.3
SELENIUM	<100	<100	<100	<100	<100	<100	<100	140	210	<137	<100	<100	<100	<100	<100
SILVER	<10	<10	<10	<10	<10	<10	20	30	50	33	20	<10	<10	120	<47

(a) EP Extract for unfixed sludge from systems I to V.
(b) EP Extract for unfixed sludge from system VI.
(c) Concentrations are in micrograms/ liter (ppb) of EP leachate.
(d) Concentrations have been blank corrected.

TABLE 10. ATTENUATION PERFORMANCE OF FIXATION SYSTEMS
METALS

ANALYTE	AVERAGE LEACHATE CONCENTRATIONS, ppb — MEASURED						AVERAGE LEACHATE CONCENTRATIONS, ppb — PREDICTED (a)						AVERAGE ATTENUATION, PERCENT						EP TOXIC LEVEL
	SYSTEM 1	SYSTEM 2	SYSTEM 3	SYSTEM 4	SYSTEM 5	SYSTEM 6	SYSTEM 1	SYSTEM 2	SYSTEM 3	SYSTEM 4	SYSTEM 5	SYSTEM 6	SYSTEM 1	SYSTEM 2	SYSTEM 3	SYSTEM 4	SYSTEM 5	SYSTEM 6	
ARSENIC	<107	<100	<100	197	363	840	<100	<100	<100	<100	<100	<3.7 (c)	---	---	---	0	0	---	5000
BARIUM	120	187	257	203	373	363	138	236	206	139	125	110	13 (b)	21	20	0	0	0	100000
CADMIUM	<5	<6	77	<6	<23	20	<8	<8	<8	<8	<9	<58	---	---	0	---	---	---	1000
CHROMIUM	180	90	100	280	100	223	32	<34	<131	40	<38	<6.8 (c)	0	0	24	0	0	---	5000
LEAD	<50	<87	1570	120	167	<60	<312	<333	12.5 (c)	387	<382	<1.4 (c)	---	---	87	69	---	---	5000
MERCURY	<0.5	<0.3	<2.1	<0.3	<0.3	<0.3	<1.2	<0.3	<1.4	<0.3	<0.3	<0.8	---	---	---	---	---	---	200
SELENIUM	<100	<100	<100	<100	<137	<100	<100	<100	<100	<100	<100	<100	---	---	---	---	---	---	1000
SILVER	<10	<10	<10	<10	33	<47	<10	<10	<10	<10	<10	<15	---	---	---	---	0	---	5000

(a) Calculated on the basis that each component contributes proportionately to the combined EP leachate.
(b) Slight differences between percentages given and those obtainable from the data shown are due to rounding.
(c) Concentration is in ppm of EP leachate.

With respect to the attenuation of metals for the first five systems, System II performed marginally better than System I with the chromium concentrations being the chief differentiating factor. System II was also somewhat better than System V for attenuation of barium, lead, and silver. Both of these were measurably better than System IV or System III. If the higher levels of arsenic, chromium and lead in the second sludge sample are taken into account, then System VI performed very creditably. On a statistical basis, however, all systems are acceptable in attenuating metals below EP toxic levels.

SUMMARY AND CONCLUSIONS

Five raw materials, two unfixed sludges and six alternative fixation systems were tested using the standard EP leaching procedure. The objective of the study was to assess the capability of each of the six alternatives to attenuate critical contaminants in the sludge. To assure that these contaminants were in fact present in the sludge, a sample of one of the sludges was exhaustively digested for metals and solvent extracted for organic compounds.

Categories of contaminants included Method 624 Volatile Priority Pollutants, 3,3' dichlorobenzidine, PCBs, 2,3,7,8 tetra-chlorodibenzodioxin, EP pesticides and herbicides and metals.

Levels of the Method 624 pollutants ranged from less than 1 ppb to in excess of 10 ppm in the raw sludge leachate. With the exception of ethylbenzene, at least one fixation system showed some attenuation of this class of analytes. System I clearly outperformed Systems IV and V and was marginally more effective than Systems II and III. The System VI initial contamination levels were considerably greater than that for the other systems. At least partly because of this fact, the attenuation percentages, while generally greater than zero, did not approach those of Systems I and III.

Dichlorobenzidine, TCDD, EP pesticides/herbicides and PCBs were not found in any leachate from unfixed or fixed materials. No conclusions can be reached regarding the performance of the fixation methods for these contaminants.

Trace amounts of metals were present in the leachate from all six systems but none exceeded the EP toxic level. The maximum percentage was observed for the System III lead concentrations which averaged 31 percent of the EP level. System II performed marginally better than System I for metal retention and, considering the high initial concentrations, System VI also was very effective. However, average attenuation for all six systems was generally low for those metals where a value could be computed.

On balance, fixation System I offered the best combination of performance on metals and volatile organic contaminants. System II was marginally better than System I for the EP metals but worse for volatile organic compounds. System III leached considerably greater amounts of lead and is intermediate to System I and II in organic compound attenuation. Systems IV and V clearly afforded the poorest performance of the systems tested with the first sludge, while System VI was the least capable overall for organic compounds but very effective for metals, disregarding the difficulties involved in comparing this system with the others.

Laboratory Procedure References

(1) EP toxicity test, Federal Register, Volume 45, No. 98, pg. 33127 (1980).

(2) Method 608 organochlorine pesticides and PCB's, Federal Register, Volume 44, No. 233, pg. 69501 (1979).

(3) 2,3,7,8-TCDD, Battelle developed in-house method currently used by several EPA Regions for soils.

(4) Method 624, purgeable organics, Federal Register, Volume 44, No. 233, pg. 69505 (1979).

(5) Method 8.8.3 metals, EPA 600/4-79-020 (1979).

(6) Method 605, benzidines, Federal Register, Volume 44, No. 233, pg. 69489 (1979).

APPENDIX A

EXTRACTION PROCEDURE (EP)

APPENDIX A

EXTRACTION PROCEDURE (EP)[a]

1. A representative sample of the waste to be tested (minimum size, 100 grams) should be obtained using the methods specified in Appendix I or any other methods capable of yielding a representative sample within the meaning of Part 260. (For detailed guidance on conducting the various aspects of the EP see "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods," SW-846, U.S. Environmental Protection Agency Office of Solid Waste, Washington, D.C. 20460.)

2. The sample should be separated into its component liquid and solid phases using the method described in "Separation Procedure" below. If the solid residue[b] obtained using this method totals less than 0.5% of the original weight of the waste, the residue can be discarded and the operator should treat the liquid phase as the extract and proceed immediately to Step 8.

3. The solid material obtained from the Separation Procedure should be evaluated for its particle size. If the solid material has a surface area per gram of material equal to, or greater than, 3.1 cm^2 or passes through a 9.5 mm (0.375 inch) standard sieve, the operator should proceed to Step 4. If the surface area is smaller or the particle size larger than specified above, the solid material should be prepared for extraction by crushing, cutting, or

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[a] United States Environmental Protection Agency, 1982, Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods. Second ed., U.S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C. SW-846.

[b] The percent solids is determined by drying the filter pad at 80° C until it reaches constant weight and then calculating the percent solids using the following equation: (weight of pad + solid) - (tare weight of pad) x 100 = % solids initial weight of sample.

grinding the material so that it passes through a 9.5 mm (0.375 inch) sieve or, if the material is in a single piece, by subjecting the material to the "Structural Integrity Procedure" described below.

4. The solid material obtained in Step 3 should be weighed and placed in an extractor with 16 times its weight of deionized water. Do not allow the material to dry prior to weighing. For purposes of this test, an acceptable extractor is one which will impart sufficient agitation to the mixture to not only prevent stratification of the sample and extraction fluid but also ensure that all sample surfaces are continuously brought into contact with well mixed extraction fluid.

5. After the solid material and deionized water are placed in the extractor, the operator should begin agitation and measure the pH of the solution in the extractor. If the pH is greater than 5.0, the pH of the solution should be decreased to 5.0 $\pm$ 0.2 by adding 0.5N acetic acid. If the pH is qual to or less than 5.0, no acetic acid should be added. The pH of the solution should be monitored, as described below, during the course of the extraction and if the pH rises above 5.2, 0.5N acetic acid should be added to bring the pH down to 5.0 $\pm$ 0.2. However, in no event shall the aggregate amount of acid added to the solution exceed 4 ml of acid per gram of solid. The mixture snould be agitated for 24 hours and maintained at 20 to 40 C (68 to 104 F) during this time. It is recommended that the operator monitor and adjust the pH during the course of the extraction with a device such as the Type 45-A pH Controller manufactured by Chemtrix, Inc., Hillsboro, Oregon 97123 or its equivalent, in conjunction with a metering pump and reservoir of 0.5N acetic acid. If such a system is not available, the following manual procedure shall be employed:

(a) A pH meter should be calibrated in accordance with the manufacturer's specifications.

(b) The pH of the solution should be checked and, if necessary, 0.5 N acetic acid should be manually added to the extractor until the pH reaches 5.0 $\pm$ 0.2. The pH of the solution should be adjusted at 15-, 30-, and 60-minute intervals, moving to the next longer interval if the pH does not have to be adjusted more than 0.5N pH units.

(c) The adjustment procedure should be continued for at least 6 hours.

(d) If, at the end of the 24-hour extraction period, the pH of the solution is not below 5.2 and the maximum amount of acid (4 ml per gram of solids) has not been added, the pH should be adjusted to 5.0 $\pm$ 0.2 and the extraction continued for an additional four hours, during which the pH should be adjusted at 1-hour intervals.

6. At the end of the 24-hour extraction period, deionized water should be added to the extractor in an amount determined by the following equation:

$V = (20)(W)-16(W)-A$

V = ml deionized water to be added

W = weight in grams of solid charged to extractor

A = ml of 0.5N acetic acid added during extraction.

7. The material in the extractor should be separated into its component liquid and solid phases as described under "Separation Procedure."

8. The liquids resulting from Steps 2 and 7 should be combined. This combined liquid (or the waste itself if it has less than 1/2 percent solids, as noted in Step 2) is the extract and should be analyzed for the presence of any of the contaminants specified in Table I of 261.24 using the Analytical Procedures designated below.

Separation Procedure. Equipment: a filter holder, designed for filtration media having a nominal pore size of 0.45 micrometers and capable of applying a 5.3 kg/cm^2 (75 psi) hydrostatic pressure to the solution being filtered shall be used. For mixtures containing nonabsorptive solids, where separation can be affected without imposing a 5.3 kg/cm^2 pressure differential, vacuum filters employing a 0.45 micrometers filter media can be used. (For further guidance on filtration equipment or procedures see "Test Methods or Evaluating Solid Waste, Physical/Chemical Methods.")

Procedure[C]

(i) Following manufacturer's directions, the filter unit should be assembled with a filter bed consisting of a 0.45-micrometer filter membrane. For difficult or slow to filter mixtures, a prefilter bed consisting of the following prefilters in increasing pore size (0.65 micrometer membrane, fine glass fiber prefilter, and coarse glass fiber prefilter) can be used.

(ii) The waste should be poured into the filtration unit.

(iii) The reservoir should be slowly pressurized until liquid begins to flow from the filtrate outlet at which point the pressure in the filter should be immediately lowered to 10 to 15 psig. Filtration should be continued until liquid flow ceases.

(iv) The pressure should be increased stepwise to 10 psi increments to 75 psig and filtration continued until flow ceases or the pressurizing gas begins to exit from the filtrate outlet.

(v) The filter unit should be depressurized, the solid material removed and weighed and then transferred to the extraction apparatus, or, in the case of final filtration prior to analysis, discarded. Do not allow the material retained on the filter pad to dry prior to weighing.

(vi) The liquid phase should be stored at 4° C for subsequent use in Step 8.

[C] This procedure is intended to result in separation of the "free" liquid portion of the waste from any solid matter having a particle size >0.45 micrometers. If the sample will not filter, various other separation techniques can be used to aid in the filtration. As described above, pressure filtration is employed to speed up the filtration process. This does not alter the nature of the separation. If liquid does not separate during filtration, the waste can be centrifuged. If separation occurs during centrifugation, the liquid portion (centrifugate) is filtered through the 0.45 um filter prior to becoming mixed with the liquid portion of the waste obtained from the initial filtration. Any material that will not pass through the filter after centrifugation is considered a solid and is extracted.

APPENDIX B

METHOD 624

VOLATILE PRIORITY POLLUTANT COMPOUNDS

APPENDIX B

Method 624

Volatile Priority Pollutant Compounds*

For the analysis of the volatile organic compounds, submethods 5030 and 8240 taken from "Test Methods for Evaluating Solid Wastes" Physical/ Chemical Methods, United States Environmental Protection Agency, July 1982, were used. The methods can be summarized as follows: 1 gram of the sample is dispersed in 20 ml of methanol. 200 ul of the methanol solution is combined with 5 ml of water in a specially designed purging chamber. Helium is then bubbled through the water solution at ambient temperature. The purgeable volatile organic compounds are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and back flushed with helium to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

Qualitative identification of the priority pollutants was performed initially using the relative retention times, the relative abundance of three characteristic ions and their ratios. The entire mass spectrum was reviewed before an identification was recorded. Quantitative analysis was performed using an internal standard with a single characteristic ion.

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* United States Environmental Protection Agency, 1982, Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, Second ed., U.S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C. SW-846.

APPENDIX C

DIOXIN ANALYSES

APPENDIX C

DIOXIN ANALYSES

The leachate samples from the EP Tox leaching were spiked with 2,3,7,8-TCDDO$^{13}C_{12}$ and liquid-liquid extracted using methylene chloride. The methylene chloride extracts were concentrated, solvent exchanged with hexane, and cleaned up using two liquid chromatography columns. The first column contained layers of concentrated sulfuric acid on silica gel and potassium silicate. It removed easily oxidized materials and the acidic and basic compounds present in the extract. This column was eluted with a 1:1 solution of benzene/hexane. The second column contained approximately 2 grams of activated alumina. It was eluted with hexane, hexane/carbon tetrachloride (1:1, v/v), and hexane/methylene chloride (1:1, v/v). The hexane/methylene chloride action was collected, concentrated, and solvent exchanged with n-decane.

The sludge sample was extracted using a mixture of hexane and methanol. Approximately 1 gram of sludge was mixed with 5 g of anhydrous sodium sulfate, spiked with 2,3,7,8-TCDD-$^{13}C_{12}$ and extracted for approximately 3 hours using the solvent mixture. The extract was filtered, concentrated, and cleaned up using the chromatography steps described above. Due to the high level of interferences in this sample, the extract was washed with concentrated sulfuric acid and 1 M potassium hydroxide solution prior to the column chromatography cleanup.

The leachate samples were analyzed by combined capillary column gas chromatography/low resolution mass spectrometry (LRMS) while the sludge sample was analyzed using high resolution mass spectrometry. A 50M CP Sil-88 fused silica capillary column was used for both the low and high resolution analyses. The two most intense ion masses in the molecular ion cluster from 2,3,7,8-TCDD and the corresponding ions from 2,3,7,8-TCDD-$^{13}C_{12}$ were monitored by the multiple ion detection (MID) technique. The quantifications were used on the response ratios of the native and isotopically labelled TCDD peaks. Thus all data are corrected for recovery losses.

A general description of the TCDD analyses for sediment and soil is included as Appendix D. The HRMS technique is described in Appendix E.*

DeRoos, F. L., 1983, Determination of TCDD in Soil and Sediment and HRMS Technique. Standard procedures of the Chemistry Department, Battelle Columbus Laboratory, Columbus, OH 43201.

APPENDIX D

DETERMINATION OF 2,3,7,8-TCDD IN SOIL AND SEDIMENT

APPENDIX D

DETERMINATION OF 2,3,7,8-TCDD IN SOIL AND SEDIMENT

I. Scope and Application

This method is intended for use in the determination of 2,3,7,8-TCDD in soil and sediment at levels of 1 part per billion (PPB) and higher. The method is specific for the 2,3,7,8-TCDD isomer, since it employs capillary columns which separate that isomer from the other 21-TCDD isomers. Total TCDD can also be estimated by this method. Determination of other specific TCDD isomers depends on the availability of the specific isomer and the separation from other interfering isomers. The final measurement process utilizes low resolution mass spectrometry. Thus, the method is a cost-effective alternative to methods requiring high resolution mass spectrometry. Because of the increased possibility for interferences at levels below 1 part per billion, the user is cautioned in extending the method range below that amount.

This method is restricted to use only by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra.

Because of the extreme toxicity of this compound, the analyst must prevent exposure to himself, or to others, by materials known or believed to contain 2,3,7,8-TCDD. Section IV of this method contains guidelines and protocols that serve as minimum safe-handling standards in a limited access laboratory.

Analyte	CAS Number
2,3,7,8-TCDD	1746-01-6

II. Summary of Method

A 10-gram sample of soil is spiked with internal and surrogate standards of isotopically labeled 2,3,7,8-TCDD. The wet sample is mixed with 20 grams of anhydrous sodium sulfate prior to extraction with hexane/ methanol using a jar extraction technique. The method provides cleanup procedures to aid in the elimination of interferences that may be encountered. The extract is concentrated to a volume of 50 uL. Capillary column GC/MS conditions are described which allow for the separation and measurement of 2,3,7,8-TCDD in the extract. Quantitation is based on the response of native TCDD relative to the isotopically labeled TCDD internal standard. Performance is assessed based on the surrogate standard results.

III. Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated backgrounds at the ions monitored. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks as described in Section VIII.

The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the sample. 2,3,7,8-TCDD is often associated with other interfering chlorinated compounds which are at concentrations several magnitudes higher than that of 2,3,7,8-TCDD. The cleanup procedures in Section XI can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to eliminate false positives and achieve the required detection limit.

The columns specified resolve 2,3,7,8-TCDD from the other 21 isomers. Positive results obtained using any other GC column must be shown to be isomer specific.

IV. Safety

The following safety practices are excerpted directly from EPA Method 613 Section 4 (July 1982 version):

In addition to the EPA Method 613 concerns, the analyst should note that finely divided dry soils contaminated with TCDD are particularly hazardous because of the potential for inhalation and ingestion of fine particulates containing TCDD. It is recommended that such samples be processed in a confined environment, such as a hood or glove box. Lab personnel handling these types of samples should also wear masks fitted with charcoal adsorbent media to prevent inhalation of dust.

Recommended field sampling safety procedures are given in Appendix C.

V. Apparatus and Materials

All glassware is initially cleaned with aqueous detergent and then rinsed with tap water, deionized water, acetone, toluene, and methylene chloride. Other cleaning procedures may be used as long as acceptable method blanks are obtained.

Grab sample bottle - glass, pint volume, fitted with screw caps lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

Clearly label all samples as "FLAMMABLE SOLID" and ship according to DOT requirements. See Appendix B for details.

Concentrator tube, Kuderna-Danish - 10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

Evaporative flask, Kuderna-Danish - 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

Snyder column, Kuderna-Danish - three-ball macro (Kontes K-503000-0121 or equivalent).

Minivials - 1.0 mL vials; cone shaped inside to enable removing very small samples; heavy wall borosilicate glass; with Teflon® faced rubber septa and screw caps.

Gas chromatograph - An analytical system complete with all required accessories including syringes, analytical columns, and gases. The injection port must be designed for capillary columns. Either split, splitless, or on-column injection techniques may be employed.

Rotary Evaporator, Rotovap R (or equivalent), Brinkmann Instruments, Westbury, N.Y.

Nitrogen blowdown apparatus, N-Evap® Analytical Evaporator Model 111 (or equivalent), Organomation Associates Inc., Northborough, MA.

Disposable pipet, 5 3/4 inches X 7.0 mm o.d., Catalog No. 14672-200, VWR Scientific, Inc., Kansas City, MO.

Columns

A. 50 m long X 0.25 mm ID glass, coated with SILAR-10C.

B. 60 m long X 0.24 mm ID fused silica capillary SP2340 (or SP2330) 0.20 u film thickness.

C. Other columns can be used as long as it is demonstrated that 2,3,7,8-TCDD is resolved from the other 21 TCDD isomers.

Mass Spectrometer - Either low resolution mass spectrometers (LRMS) or high resolution mass spectrometers (HRMS) may be used. The mass spectrometer must be equipped with a 70 volt (nominal) ion source and be capable of acquiring ion abundance data in real time Selected Ion Monitoring (SIM) for groups of six or more ions. The electron impact ionization mode must be used.

GC/MS interface - Any gas chromatograph to mass spectrometer interface can be used that achieves the requirements of Section VIII. Glass or glass-lined materials are recommended. Glass surfaces can be deactivated by silanizing with dichlorodimethylsilane. To achieve maximum sensitivity, the exit end of the capillary column should be placed in the ion source. A short piece of fused silica capillary can be used as the interface to overcome problems associated with straightening the exit end of glass capillary columns.

The SIM data acquired during the chromatographic program can be acquired under computer control or as real time analog output. If computer control is used, there must be software available to plot the SIM data and report peak height or area for any ion between specified time or scan number limits.

Balance - Analytical, capable of accurately weighing 0.0001 g.

VI. Reagents

All TCDD standard solutions utilized must be verified by comparison to 2,3,7,8-TCDD check standard solutions available from EPA (Environmental Monitoring Systems Lab - Las Vegas). The stock check standard solution will be provided at a concentration of 7.87 ug/mL (7.87 ng/uL) in isooctane. Surrogate and internal standard solutions of $^{37}Cl_4$ 2,3,7,8-TCDD (mol wt 328) and $^{13}C_{12}$ 2,3,7,8-TCDD (mol wt 332), respectively, can be prepared from pure standard materials or purchased as solutions. These standards can be obtained from commercial sources (KOR Isotopes, Fifty-six Rogers Street, Cambridge, MA 02142 and Cambridge Isotope Laboratories, Inc., 141 Magazine Street, Cambridge, MA 02139). The standards should be analyzed to verify the absence of contribution of native 2,3,7,8-TCDD. Prepare a stock internal standard solution of $^{13}C_{12}$ 2,3,7,8-TCDD at 2.5 ng/uL in isooctane by appropriately diluting the commercial standard which is supplied at 50 ng/uL

in anisole. Prepare a stock surrogate standard solution of $^{37}Cl_4$-2,3,7,8-TCDD at 2.0 ng/uL in isooctane by appropriately diluting the commercial standard which is also supplied at 50 ng/ul in anisole.

Calibration Standards

The calibration standard solutions contain constant amounts of internal standard (2.5 PPB equivalent) and surrogate standard (1.0 PPB equivalent) with variable amounts of native standard. The described solutions are equivalent to native TCDD concentrations of 25, 5, and 1 PPB ~~for 10-gram~~ samples with 50 uL extract volumes. Some samples may require extending the calibration range beyond 25 PPB. This will require the use of commercially supplied native TCDD standards. Additional calibration standards equivalent to 100 PPB (20 ng/uL of native TCDD) and 200 PPB (40 ng/uL) are recommended. Both should contain the internal standard TCDD at 500 pg/uL. It is not necessary to add the surrogate standard to these higher level standards.

High Level (25 PPB Equivalent for native TCDD)

Combine 127 uL of the stock native TCDD standard (7.87 ng/uL), 20 uL of the $^{37}Cl_4$ 2,3,7,8-TCDD surrogate standard (2.0 ng/uL), and 40 uL of the $^{13}C_{12}$ 2,3,7,8-TCDD internal standard (2.5 ng/uL) in a 1-mL minivial. Add 13 uL of isooctane and mix well. The mix contains native TCDD at 5.0 ng/uL, surrogate standard - TCDD ($^{37}Cl_4$) at 200 pg/uL and internal standard TCDD ($^{13}C_{12}$) at 500 pg/uL.

Medium Level (5 PPB Equivalent for native TCDD)

Combine 40 uL of the high level solution 32 uL of the internal standard ($^{13}C_{12}$ at 2.5 ng/uL) and 16 uL of the surrogate standard ($^{37}Cl_4$ at 2.0 ng/uL) in a 1-ml minivial. Add 112 uL of isooctane and mix well. The mix contains native TCDD at 1.0 ng/uL surrogate standard - TCDD ($^{37}Cl_4$) at 200 pg/uL and internal standard - TCDD ($^{13}C_{12}$) at 500 pg/uL.

Low Level (1.0 PPB Equivalent for native TCDD)

Combine 40 uL of the medium level solution with 32 uL of the internal standard ($^{13}C_{12}$ at 2.5 ng/uL) and 16 uL of the surrogate standard ($^{37}Cl_4$ at 2.0 ng/uL) in a 1-mL minivial. Add 112 uL of isooctane and mix well. The mix contains native TCDD at 200 pg/uL, surrogate standard at 200 pg/uL, and internal standard at 500 pg/uL.

Spiking Standard Solutions

The spiking solution contains both internal standard and surrogate standard.

Add 1.0 mL of the $^{13}C_{12}$ 2,3,7,8-TCDD internal standard stock solution (2.5 ng/uL), and 0.5 mL (500 uL) of the $^{37}Cl_4$ 2,3,7,8-TCDD surrogate standard stock solution (2.0 ng/uL) to a 10-mL volumetric flask. Dilute

to volume with isooctane. Mix well. The solution has a concentration of 250 ng/mL of internal standard and 100 ng/mL of surrogate standard. 100 uL aliquots are used for dosing samples.

Column Performance Solution

Each vial containing the column performance mixture contains approximately 50 to 100 nanograms each of seven TCDD isomers (2378, 1478, 1234, 1237, 1238, 1278, and 1267). To the solid mixture add 250 microliters of the spiking standard solution containing 250 pg/uL of internal standard and 100 pg/uL of surrogate standard. The approximate concentrations of unlabeled TCDD isomers will thus be in the range of 200 to 400 pg/uL.

All standards must be stored in an isolated refrigerator and protected from light.

Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards or spiking solutions from them.

Calibration standard solutions must be replaced after six months.

Sulfuric Acid (Conc.) - (ACS) sp. gr. 1.84.

Methylene chloride, hexane, benzene, methyl alcohol, tetradecane, and other solvents - pesticide quality or equivalent.

Sodium sulfate - (ACS) Granular, anhydrous (purified by heating at 400°C for four hours in a shallow tray or methylene chloride extraction).

Silica gel - for column chromatography, type 60, EM Reagent, 100-200 mesh, or equivalent. Soxhlet extract with methylene chloride, and activate in a foil covered glass container for 24 hours at 130°C.

Alumina - acidic, AG-4, Bio-Rad Laboratories (catalog No. 132-1240 or equivalent), Soxhlet extract with methylene chloride, and activate in a foil covered glass container for 24 hours at 190°C.

Alumina - basic, Woelm activity grade I or equivalent (activate at 600°C for 24 hours), ICN Nutritional Biochemicals, Cleveland, Ohio.

Sulfuric acid - impregnated silica gel (40% w/w) - add two parts concentrated sulfuric acid to three parts silica gel in a screw capped bottle and mix with a glass rod until lump free. Carbopak C, 80/100 mesh, catalog no. 1-0258, Supelco, Inc., Bellefonta, PA. Celite 545®, not acid washed, catalog no. C-212, Fisher Scientific Company, Pittsburg, PA.

VII. Calibration

Calibration must be done using the internal standard technique. By injecting calibration standards, establish ion response factors for

2,3,7,8-TCDD vs. the internal standard ($^{13}C_{12}$ 2,3,7,8-TCDD), and for the surrogate standard ($^{37}Cl_4$ 2,3,7,8-TCDD) vs. the internal standard ($^{13}C_{12}$ 2,3,7,8-TCDD). Using stock standards, prepare GC/MS calibration standards as described in Section VI. Standard solutions equivalent to 1, 5, and 25 PPB are required for routine work. Additional standard solutions at 100 and 200 PPB may be required.

Using injections of 1 to 3 uL, tabulate peak height or area response against the concentration of 2,3,7,8-TCDD vs. internal standard and $^{37}Cl_4$ 2,3,7,8-TCDD vs. internal standard and calculate relative response factors (RRF) for both native TCDD and surrogate standard TCDD using Equations 1 and 2.

Equation 1 (RRF for native 2,3,7,8-TCDD)

$$RRF = (AsCis)/(AisCs)$$

where: As = SIM response for 2,3,7,8-TCDD (m/e 320 + 322)
Ais = SIM response for $^{13}C_{12}$ 2,3,7,8-TCDD internal standard (m/e 332 + 334)
Cis = Concentration of the internal standard (pg/ul)
Cs = Concentration of 2,3,7,8-TCDD (pg/uL)

Equation 2 (RRF for surrogate standard, $^{37}Cl_4$ 2,3,7,8-TCDD)

$$RRF = (AssCis)/(AisCss)$$

where: Ass = SIM response for $^{37}Cl_4$ 2,3,7,8-TCDD (m/e 328)*
Ais = SIM response for $^{13}C_{12}$ 2,3,7,8-TCDD internal standard (m/e 332 + 334)
Cis = Concentration of the internal standard (pg/uL)
Css = Concentration of the surrogate standard $^{37}Cl_4$ 2,3,7,8-TCDD (pg/uL)

*When using $^{37}Cl_4$-TCDD, correct the 328 response by subtracting 0.009 of the 322 response.

The RRF Values over the working range for native TCDD must be demonstrated to be constant (<10% RSD). The average RRF must be used for calculations. The RRF must be verified on each work shift of 8 hours or less, by the measurement of one or more calibration standards (one must be a 1.0 PPB standard). If the response for 2,3,7,8-TCDD varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration must be preformed.

The surrogate standard RRF must be determined from the same set of three calibration standards which contain a constant amount (1.0 PPB equivalent) of surrogate standard. The surrogate RRF must also be verified on each work shift of eight (8) hours or less. If the response varies by more

than ± 10% from the predicted response, the test must be repeated or a new calibration must be performed for the surrogate compound.

The most recent verified RRF (mean of results from 3-point calibration) must be used in all calculations.

VIII. Quality Control Requirements

1. Each sample must be dosed with a known quantity of internal standard (equivalent to 2.5 PPB) and surrogate standard (equivalent to 1.0 PPB).

The action limits for surrogate standard results will be ± 40% of the true value. Samples showing surrogate standard results outside of these limits must be reextracted and reanalyzed.

2. A laboratory "method blank" must be run along with each set of 24 or fewer samples. A method blank is performed by executing all of the specified extraction and cleanup steps, except for the introduction of a 10-gram sample. The method blank is also dosed with the internal standard and surrogate standard.

3. The laboratory will be given performance evaluation samples by EPA on a periodic basis throughout the course of a given project. Additional sample analyses will not be permitted if the performance criteria are not achieved. Corrective action must be taken and demonstrated before sample analyses can resume.

4. Samples will be split with other participating labs on a periodic basis to ensure interlaboratory consistency.

5. At least one per set of 24 samples must be run in duplicate to determine intralaboratory precision.

6. Field duplicates (individual samples taken from the same location at the same time) will be submitted periodically to determine the total precision (field and lab).

7. Qualitative Requirements. The following requirements must be met in order to confirm the presence of native 2,3,7,8-TCDD:

a. Isomer specificity must be demonstrated initially and verified once per 8-hour work shift. The verification consists of injecting a mixture containing TCDD isomers which elute close to 2,3,7,8-TCDD. This mixture will be provided by EPA. It contains seven TCDD isomers (2378, 1478, 1234, 1237, 1238, 1278, 1267) including those isomers which are known to be the most difficult to separate on SP2330/SP2340 columns and similar columns containing cyanoalkyl type liquid phases. The column performance solution (Section VI) must also contain both isotopically

labeled 2,3,7,8-TCDD standards. The solution must be analyzed using the same chromatographic conditions and mass spectrometric conditions as is used for other samples and standards. The 2,3,7,8-TCDD must be separated from interferring isomers, with no more than a 25% valley relative to the 2,3,7,8-TCDD peak.

Draw a baseline for the isomer cluster representing 1478, 2378, 1237, 1238, and 1234-TCDD. Measure the distance x from the baseline to the valley following the 2,3,7,8-TCDD peak (use the valley preceding the 2,3,7,8-TCDD peak if it is higher). Measure the distance y from the baseline to the apex of the 2,3,7,8-TCDD peak. Distance x over distance y times 100 is the percent valley which must not exceed 25. An example is given in Figure 1.

b. The 320/322 ratio must be within the range of 0.67 to 0.87.

c. Ions 320, 322, and 257 must all be present and maximize together. The signal to mean noise ratio must be 2.5 to 1 or better for all 3 ions. (Determine the noise level by measuring the random peak to valley signal present on either side [within 20 scans] of the 2,3,7,8-TCDD retention window. The 2,3,7,8-TCDD signal must be at least 2.5 times larger than this.)

d. The retention time must equal (within 3 seconds) the retention time for the isotopically labeled 2,3,7,8-TCDD.

e. At least one of the positive samples per set of 24 total samples must be confirmed by high resolution mass spectrometry (resolution of 10,000 or better). Alternately, one of the positives can be confirmed by obtaining partial scan spectra from mass 150 to mass 350. The partial scan guidelines are as follows:

- the 320/324 ratio should be 1.58 $\pm$ 0.16
- the 257/259 ratio should be 1.03 $\pm$ 0.10
- the 194/196 ratio should be 1.54 $\pm$ 0.15
- ions 160, 161, 194, 196, 257, 259, 320, 322, and 324 should all be present with at least 5% relative abundance (relative to 322)

8. One sample must be spiked with native 2,3,7,8-TCDD at a level of 1.0 PPB for each set of 24 or fewer samples. EPA will designate the sample to be dosed.

9. In cases where no native 2,3,7,8-TCDD is detected, the actual detection limit must be estimated and reported based on a signal to noise ratio of 2.5 to 1 at ions 320 and 322. Measure the mean noise for the retention window* of 2,3,7,8-TCDD for the 320 + 322 mass chromatogram. Multiply the noise by 2.5 and calculate the detection limit according to Equation 3

in Section XII. If an interfering signal is present at 320 or 322, choose the ion not interfered with to calculate a detection limit using Equation 3 (use responses for 320 and 332 or 322 and 334.) If both ions have interferences which are more than 2.5 times the noise, compute the detection limit using Equation 3 (use the summed response of 320 and 322, but do not multiply by 2.5).

*The retention window is defined as the period of elution for the internal standard (ions 332 and 334) starting at the point where the signal first exceeds 2.5 times the noise and ending at the point where the signal last exceeds 2.5 times the noise.

10. For each sample, the internal standard must be present with at least a 10 to 1 signal to noise ratio for both mass 332 and mass 334. Also, the internal standard 332/334 ratio must be within the range of 0.67 to 0.87.

11. Where appropriate, "field blanks" will be provided to monitor for possible cross contamination of samples in the field. The "field blank" will consist of uncontaminated soil (background soil taken off-site) and/or equipment rinsate (field equipment such as augers which have been rinsed with trichloroethylene or other solvent).

IX. Sample Extraction (Jar Method)

CAUTION: When using this method to analyze for 2,3,7,8-TCDD, all of the following operations should be performed in a limited access laboratory with the analyst wearing full protective covering for all exposed skin surfaces. See Section IV for details on specific safety requirements.

1. Transfer a 10-gram (10 to 12 grams weighed to 3 significant figures) aliquot of sample directly into the extraction jar.

2. Add 100 uL of spiking standard solution (containing both internal and surrogate standards). The solution will contain 250 ng/mL of internal standard and 100 ng/mL of surrogate standard. Add the 100 uL solution chosen directly to the soil, spreading it over several sites on the surface of the soil.

3. Add 20 grams of purified anhydrous sodium sulfate and mix thoroughly using a stainless steel spoon or spatula. (Extremely wet samples may require prior centrifugation to remove excess water; see phase separation, this section.) Allow the mixture to stand under ambient conditions. Mix again after 2 hours and allow to stand for at least 6 additional hours. (The soil/sodium sulfate mixture must be free of lumps before proceeding.) Mix again just before adding solvent.

4. Add 20 mL of methanol, stir, and then add 150 mL of hexane.

5. Extract the sample vigorously for a minimum of 3 hours. A wrist action shaker, platform shaker, magnetic stirrer, or equivalent device may be used.

6. Allow the solids to settle before proceeding.

7. Carefully decant the extract through a glass funnel fitted with solvent rinsed filter paper (Whatman No. 4 or equivalent). Thoroughly rinse the extraction jar, its contents, and the filter residue with hexane. Alternately, the extract can be transferred by pipetting.

8. Concentrate the extract to 1.0 mL using Kuderna-Danish, nitrogen blowdown, or rotary evaporator techniques. When using rotary evaporator concentration techniques, care must be taken to carefully rinse the apparatus between samples to prevent cross contamination of samples. The extract is now ready for cleanup as described in Section XI.

Phase Separation

This is a guideline for phase separation on very wet soil samples. Every type of sample has not been tried using this methodology. Special treatment may be needed to achieve adequate results.

Place 30-gram aliquot in a suitable centrifuge bottle. Then place sample and counter-balance in centrifuge. Run for 30 minutes at 2,000 rpm. Stop.

Remove. Mark interface levels on bottle. Estimate relative volume of each phase. Using disposable pipets, transfer liquid layer into clean bottle. Analyze the solid phase only using this soil/sediment method.

Rinsate Samples

As mentioned in Section VIII, field blanks consisting of solvent rinsate will be provided to monitor for cross-contamination of samples in the field. The liquids should be handled as follows:

1. To a 100 mL aliquot of solvent rinsate (typically technical grade trichloroethylene) add 100 uL of a low level spiking standard containing 250 ng/mL of $^{13}C_{12}$ TCDD internal standard and 100 ng/mL of $^{37}Cl_4$-TCDD surrogate standard.

2. Concentrate the solution to approximately 5 mL. Add 1.0 mL of isooctane and further concentrate to less than 1.0 mL.

3. Adjust the volume to 1.0 mL using isooctane.

4. Continue the analysis as described in Section XI.

5. If 2,3,7,8-TCDD is detected, immediately notify the client so that corrective action can be taken.

X. Cleanup Procedures

Cleanup procedures are necessary for all samples. Additional cleanup must be performed if any of the following conditions are observed:

1. The sample extract can not be concentrated to 50 uL volume.

2. Interferences prevent observation of either of the isotopically labeled 2,3,7,8-TCDD standards.

3. Interferences are present in the retention time window at mass 320 or 322 or 257.

4. The required detection limit of 1.0 PPB can not be achieved.

5. The sample extract is colored or cloudy, viscous, or contains a precipitate.

The following cleanup options are recommended. Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

Option A

1. Pack a 1 X 10 cm chromatography column with 1.0 g of silica gel* and 4.0 g of 40% w/w sulfuric acid-modified silica gel. Pack a second chromatography column (1 X 30 cm) with 6.0 g of alumina* and a 1-cm layer of sodium sulfate. Add hexane to the columns until free of channels or air bubbles. This can be readily achieved using a small positive pressure (5 psi) of clean nitrogen.

*Silica gel (for column chromatography, type 60, EM Reagent, 100-200 mesh) and alumina (acid alumina, AG 4, BIO-RAD Laboratories) are Soxhlet-

extracted with CH_2Cl_2 for 21 hours and activated at 130°C and 190°C, respectively, before use. Each batch should be tested for proper recovery of 2,3,7,8-TCDD prior to use.

2. Place the hexane extract on top of the silica gel and rinse the culture tube with 2 X 0.5 mL of hexane onto the column and elute directly onto the alumina column with 45 mL of hexane. Discard the silica gel.

3. Place 20 mL of hexane on the alumina column and elute until the liquid has dropped below the sodium sulfate layer. Discard the eluted hexane.

4. Place 20 mL of 20% v/v methylene chloride/hexane solution on top of the alumina. Collect this fraction in a 125-ml Erlenmeyer flask.

5. The volume of this eluate which contains TCDD is reduced by a gentle stream of filtered nitrogen gas. When the volume is down to about 1-2 mL, aliquots are transferred, one at a time, to a 2-mL conical mini vial for further concentration until the entire fraction is transferred. One mL of hexane is used to rinse the Erlenmeyer flask and is transferred, in portions, to the mini vial. Repeat this procedure once more. At no time must the extract be allowed to go to dryness. Finally 500 uL of hexane is used to rinse the walls of the mini vial. The sample is stored at this point in a freezer until analysis. Just before analysis begins, the hexane volume is reduced to almost dryness and isooctane (or other C_8 to C_{14} hydrocarbon) is added to obtain a final volume of 50 uL.

Option B

1. Prepare a glass macro-column, 20 mm OD X 230 mm in length, tapered to 9 mm OD on one end. Pack the column with a plug of silanized glass wool, followed successively by 1.0 g silica gel, 2.0 g silica gel containing 33% (w/w) 1M NaOH, 1.0 g silica gel, 4.0 g silica gel containing 44% (w/w) concentrated H_2SO_4 and 2.0 g silica gel. Add hexane to the columns until free of channels or air bubbles. Quantitatively transfer the concentrated sample extract to the column and elute with 90 mL hexane. Collect the entire eluate and concentrate to a volume of <1 mL in a centrifuge tube.

2. Construct a chromatography column by packing a 5 mL disposable pipet (cut off at the 2.0 mL mark) with a plug of silanized glass wool and add 1 gram of activated Woelm basic alumina (activated at 600° for 24 hours) to the tube.

3. Quantitatively transfer the concentrated extract from Step 1 to the top of the column using 2 mL hexane.

4. Elute the column with 5 mL of 3% methylene chloride-in-hexane and discard the eluate.

5. Elute the column with 20 mL of 50% methylene chloride-in-hexane and retain the entire column eluate for analysis.

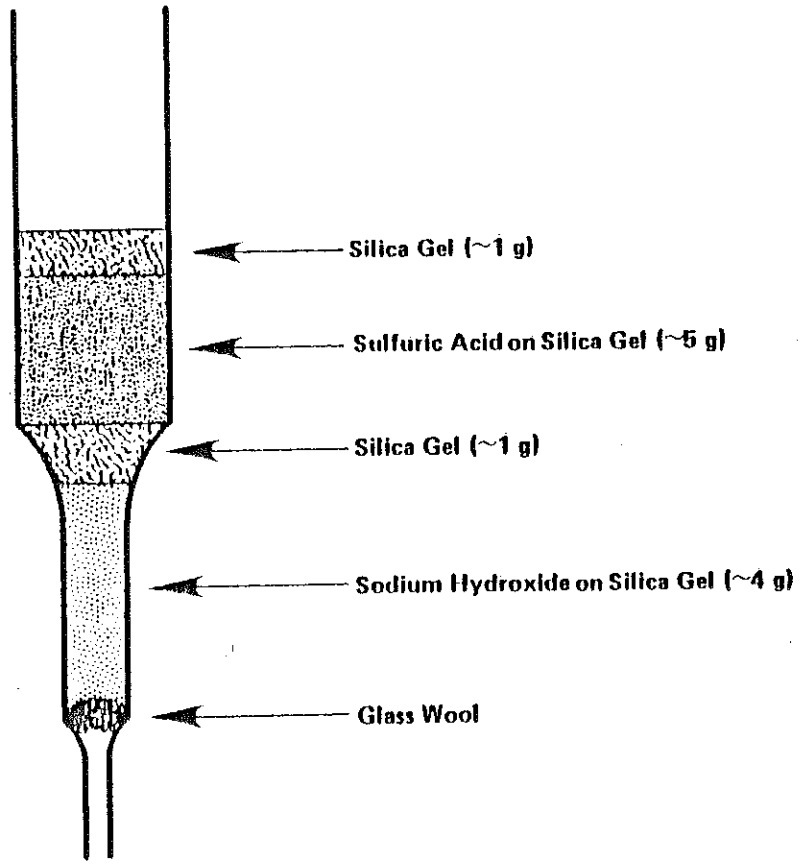

FIGURE D-1. MULTILAYERED SILICA COLUMN

6. Concentrate the eluate from a volume <1 mL and quantitatively transfer it to a 2 mL conical minivial.

7. Further concentrate the extract in the mini-vial to near dryness, and store the extract at 5°C until just prior to GC/MS analysis.

8. Prior to GC/MS analysis, reconstitute the extract by adding isooctane (or other C_8 to C_{14} hydrocarbon) and adjusting the final volume to 50 uL.

Option C

Certain very dirty samples may require preliminary cleanup prior to column chromatography. For those situations, the following procedure is suggested:

1. Wash the organic extract with 30 mL of 20% aqueous potassium hydroxide by shaking for 10 minutes and then remove and discard the aqueous layer.

2. Wash the organic extract with 25 mL of doubly distilled water by shaking for 2 minutes and again remove and discard the aqueous layer.

3. CAUTIOUSLY add 50 mL concentrated sulfuric acid to the organic extract and shake for 10 minutes. Allow the mixture to stand until the aqueous and organic layers separate (approximately 10 minutes) and remove and discard the aqueous acid layer. Repeat acid washing until no color is visible in the acid layer.

4. Add 25 mL of doubly distilled water to the organic extract and shake for 2 minutes, remove and discard the aqueous layer and dry the organic layer by adding 10 g of anhydrous sodium sulfate.

5. Transfer the organic extract to a centrifuge tube and concentrate to near dryness by placing the tube in a water bath at 55°C, while passing a gentle stream of filtered, prepurified N_2 over the surface of the extract.

Reconstitute in hexane before proceeding with the column chromatography (Option A or B).

Option D

Certain extracts, even after cleanup by column chromatography, contain interferences which preclude determination of TCDD down to 1.0 parts per billion. The cleanup described here is to be used after Option A or Option B. The method uses activated carbon which selectively retains planar molecules such as TCDD. The TCDD is removed by elution with toluene.

Prepare 18% Carbopak C on Celite 545® by thoroughly mixing 3.6 grams of Carbopak C (80/100 mesh) and 16.4 grams of Celite 545® in a 40-ml vial. Activate at 130°C for six hours. Store in a desiccator. Prepare a column using a standard size (5-3/4 inches long by 7.0 mm o.d.) disposable pipet fitted with a small plug of glass wool. Using a vacuum aspirator attached

to the pointed end of the pipet, add the carbopak/celite mix until a 2 cm column is obtained. Preelute the column with 2-ml of toluene followed by 1-ml of 75:20:5 methylene chloride/methanol/benzene, 1-ml of 1:1 cyclohexane in methylene chloride and 2-ml of hexane. While the column is still wet with hexane add the 50 microliter extract obtained from Option A or Option B. Elute the column sequentially with two 1-ml aliquots of hexane, 1-ml of 1:1 cyclohexane in methylene chloride, and 1-ml of 75:20:5 methylene chloride/methanol/benzene. Next collect the TCDD fraction by elution with 2-ml of toluene. The sample is stored at this point in a freezer until GC/MS analysis. Just before analysis begins, reduce the volume to near dryness and add isooctane to obtain a final volume of 50 uL.

NOTE: Each new batch of carbopak/celite must be checked to insure that the TCDD recovery is adequate. Subject the low level calibration standard to this procedure. A native TCDD recovery of at least 50% is required.

XI. GC/MS Analysis

1. Immediately before analysis by GC/MS, adjust the sample extract volume to approximately 50 uL.

2. Table I summarizes typical gas chromatographic capillary columns and operating conditions. Other columns and/or conditions may be used as long as isomer specificity is demonstrated. Thereafter a calibration mixture of isomers should be analyzed on a daily basis in order to verify the performance of the system (see Section VIII for criteria).

3. Analyze standards and samples with the mass spectometer operating in the selected ion monitoring (SIM) mode using a scan time to give at least five points per peak. For LRMS, use ions at m/e 320, 322, and 257 for 2,3,7,8-TCDD, m/e 328 for $^{37}Cl_4$ 2,3,7,8-TCDD, and ions at m/e 332 and 334 for $^{13}C_{12}$ 2,3,7,8-TCDD. For HRMS, use ions at m/e 319.8965 and 321.8936 for 2,3,7,8-TCDD, ion at m/e 327.8847 for ^{37}Cl 2,3,7,8-TCDD, and ion at m/e 331.9367 for ^{13}C 2,3,7,8-TCDD.

4. Calibrate the system daily as described in Section VII. The volume of calibration standard injected should be approximately the same as all sample injection volumes. The requirements described in Section VIII, Parts 7b, 7c, and 7d must be met for all calibration standards.

5. Inject a 1 to 3 uL aliquot of the sample extract.

6. The presence of 2,3,7,8-TCDD is qualitatively confirmed if the criteria of Section VIII, Part 7, are achieved.

7. For quantitation, measure the response of the m/e 320 and 322 peaks for 2,3,7,8-TCDD, the m/e 332 and 334 peaks for $^{13}C_{12}$ 2,3,7,8-TCDD, and the 328 peak for $^{37}Cl_4$ 2,3,7,8-TCDD. A correction must be made for contribution to m/e 328 by any native TCDD which may be present. To do this, subtract 0.009 of the 322 response from the 328 response. Calculate the concentration of

1. The sample identification number.

2. The calculated value for native 2,3,7,8-TCDD. (Values below 1.0 PPB are also reported.)

3. If no 2,3,7,8-TCDD was detected, report "not detected" or N.D. and give the calculated detection limit. (Detection limits below 1.0 PPB are also reported.)

4. The raw peak responses for ions 320, 322, 257, and 328 or 332 and 334.

5. The response ratio of 320/322 and 332/334.

6. Analytical date and time.

7. The percent accuracy for the surrogate standard.

8. The results of duplicate analyses.

9. The percent recovery of native TCDD from spiked samples.

10. The results from the method blanks.

11. Response factors for the three point calibration (for both native TCDD and isotopic surrogate standard).

12. The daily verification of the response factors including one at 1.0 PPB.

13. The mass chromatograms for the daily column performance check.

14. The mass chromatograms for all samples and standards. Include any computer generated response tables.

15. The weight of the original wet sample aliquot.

16. Documentation on the source of the native and labeled 2,3,7,8-TCDD standards used.

17. A reconstructed ion chromatogram for any partial scan confirmation runs.

18. Any other supporting documentation.

An example of the required data report format follows:

TCD [illegible]

Lab: _____

Case: _____

Date: _____

GC Column: _____

RF Native: _____

RF Surrogate: _____

Sample Number	Extraction Method	Cleanup Option	Grams Wet Weight	PPB TCDD	D.L.	Analytical Date	Analytical Time	320/322	332/334	Surrogate Percent Accuracy	320	322	257	328†	332	334	Comments
861	J	A	11.2	28	--	6/03	12:00	0.79	0.78	102	354,229	449,175	34,000	90,269	41,516	53,225	--
862	J	A	10.5	ND	0.3	6/03	1:00	1.00	0.78	89	900	900	45	62,002	48,960	62,769	Isotope Ratio out of acceptable range
861D	J	A	10.9	24	--	6/03	2:00	0.78	0.78	95	93,381	120,055	32,000	54,918	27,278	34,971	--
MB	J	A	--	ND	0.2*	6/03	3:00	--	0.78	101	0	0	80	58,139	22,108	28,343	--

†Corrected for contribution by native TCDD (Subtract 0.009 of m/e 322).

*Based on 10 gram sample.

MB = Method Blank
P = Partial Scan
N = Native TCDD Spike
D = Duplicate (Intralab)
FB = Field Blank

H = High Resolution
ND = Not Detected
DL = Detection Limit
J = Jar

A,B,C - Cleanup Option (or any combination)

TCDD Data Report - Page 2

CALIBRATION SUMMARY

ug/kg* Native TCDD	RRF (Native)	Date	Time	RRF (Surrogate)	Instrument Designation
1.0	0.60	12/3		0.70	
5.0	0.59	12/3		0.69	
25.0	0.61	12/3		0.71	
1.0	0.62	12/4		0.68	
1.0	0.60	12/5		0.72	

*Assumes 10 gram sample.

QUALITY CONTROL SUMMARY

Item	# of Data Points	Mean ± S.D.
Surrogate Accuracy	24	100 ± 15%
Native TCDD Recovery	1	85%

EPA Surrogate Action Limits: 60-140% (0.6-1.4 PPB)

TCDD Data Report - Page 3

Partial Scan Confirmation

Sample Number	Response Ratios			% Relative Abundances*								
	320/324	257/259	194/196	160	161	194	196	257	259	320	322	324
861F	1.53	1.06	1.44	13	13	23	16	36	34	84	100	55

*Relative to m/e 322.

XIV. Sample Reruns

Sample analyses must be repeated if any of the following conditions apply:

1. A detection limit of 1.0 PPB could not be achieved. Subject the extract to additional cleanup. Use Option D.

2. The percent accuracy for surrogate standard was outside of acceptance limits. Reextract and reanalyze sample aliquot. Use Option B followed by D.

3. The calculated TCDD amount was outside the upper calibration range. Extend the calibration range by running an appropriate standard or reextract using a 1.0 gram sample aliquot.

4. The method blank contained TCDD. Reanalyze the entire batch of samples.

5. The internal standard 332/334 ratio was outside the 0.67-0.87 control limits. Subject the extract to additional cleanup. Use Option D.

6. The internal standard was not present with at least 10/1 signal to noise ratio at mass 332 and 334. Reextract and reanalyze sample aliquot. Use Option A or B followed by D.

TABLE I

Recommended GC Capillary Conditions

Column	A (Silar 10C)	B (SP2340)
2,3,7,8-TCDD R.T.	34.5 min	22 min
Helium Linear Velocity	30 cm/sec	0.7 ml/min at 60°C
Initial Temperature	100°C	60°C
Initial Time	3.0 min	3 min
Splitless Time		1.0 min
Program Rate	20°C/min	25°C/min
Final Temperature	180°C*	250°C
Final Hold Time	15 min	15 min
Split Flow		30 ml/min
Septum Purge Flow		5 ml/min
Capillary Head Pressure		30 psi

*then 2°/min to 250°C

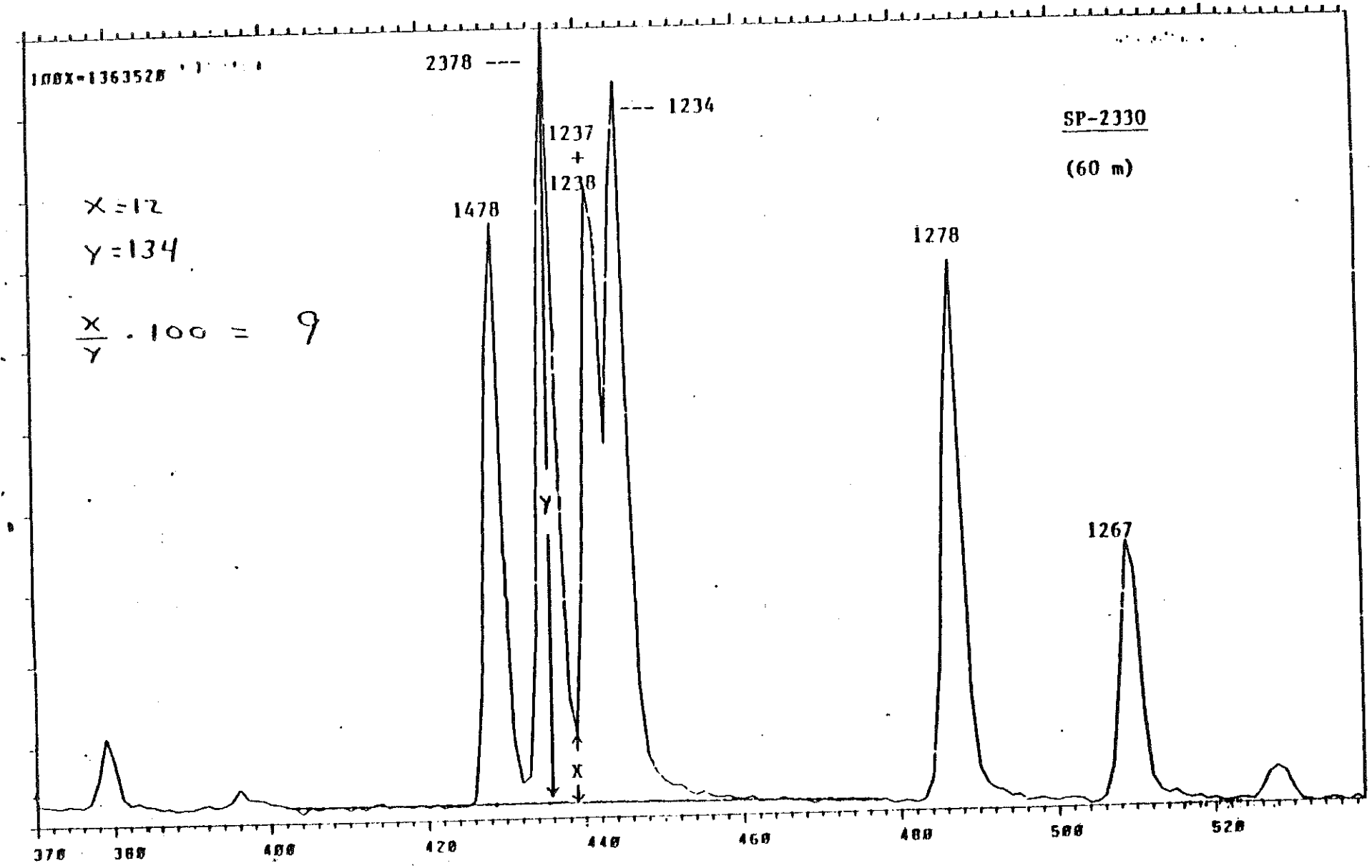

Figure 1. Selected ion current profile for m/z 320 and 322 produced by MS analysis of performance check solution using a 60-m SP-2330 fused silica capillary column.

APPENDIX E

HRMS METHOD DESCRIPTION

APPENDIX E

HRMS METHOD DESCRIPTION

Combined capillary column gas chromatography/low resolution mass spectrometry (HRGC/LRMS) is a proven technique for the trace level determination of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). The selectivity of capillary column gas chromatography combined with the sensitivity of mass spectrometry affords detection limits of these dioxins and furans in the range of 0.5-2 parts-per-billion (ppb, w/w). Certain compounds, such as polychlorinated biphenyls (PCB), can interfere with PCDD/PCDF analyses by low resolution mass spectrometry. For example, heptachlorobiphenyl isomers readily lose two chlorine atoms under electron impact ionization to produce an ion of nominal mass-to-charge ratio (m/z) 322. The ion at m/z 322 is also the molecular ion for tetrachlorinated dioxin isomers (TCDD) which is monitored for their measurement. Furthermore, the heptachlorobiphenyls elute from the GC column with similar retention times to the TCDD isomers. If the sample contains PCB levels in the range of 10-1,000 parts-per-million, these materials will interfere with the measurement of tetrachlorinated dioxins and detection limits at the part-per-billion level will not be possible.

Combined high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) is used to resolve PCB interferences to the PCDD/PCDF measurement. Operating the mass spectrometer at 10,000-12,000 mass resolution ($M/\Delta M$, 10% valley) separates the exact masses of the dioxin and furan compounds from the PCB materials at a specific nominal m/z value. Isolation of the dioxin and furans from impurities by mass resolution improves their detection limit to allow for measurement in the 1-10 parts-per-trillion (ppt) range.

The following sections describe the complete analysis of a sample by high resolution GC/MS through a typical progression from sample eceipt, extraction, compound class isolation, analysis and reporting.

Receipt of Samples

Establishment of sample chain of custody is extremely important for all samples submitted for PCDD/PCDF analysis. Due to the potential impact of the analytical results, such as health concerns or termination of an industrial process, it is mandatory to maintain a record documenting the history of each sample which enters the PCDD/PCDF facility. This documentation, which is entered into a bound laboratory notebook, includes the sponsor requesting the analysis, the sponsor's sample identification number, the date the sample was received, the sample matrix, and the condition of the sample. Each sample is assigned a unique identification number which follows the sample through the analysis procedure.

Extraction

Samples are spiked with one or more isotopically labelled dioxin and/or furan internal standards followed by an efficient solvent extraction to remove the incorporated native PCDD/PCDF. Although the spiking of a sample with internal standards is often treated as an invariant, it can cause gross inaccuracies in the quantifications and requires careful attention. The internal standards must be spiked into the sample in such a way that they realistically correct for recovery efficiencies. When using the Soxhlet technique for example, the top portion of the extractor should be manually filled with the extraction solvent and the internal standards spiked into the solvent. The extractor should be allowed to equilibrate for approximately one hour before the extraction is started. This will allow the internal standards to interact with the sample matrix and approximate the adsorption charactistics of the native PCDD/PCDF.

Aqueous samples are less difficult to spike. They must, however, be spiked with the internal standards dissolved in a water miscible solvent. A technique that we employ is to add the internal standard (typically in decane) to approximately 2 ml of acetone. After equilibrating this solution for approximately 30 minutes, it is quantitatively transferred to the aqueous sample.

The optimum extraction method and solvent depend on the particular sample matrix. The method must be sufficiently complete to insure efficient extraction of the native PCDD/PCDF, yet not extract significant qualities of the sample matrix. A list of selected matrices and the recommended extraction methods and solvents is provided in Table 1.

Removal of Coextracted Interferences

The extraction procedure removes a variety of compounds in addition to PCDD/PCDF, such as pesticides and PCB which can potentically interfere with the analysis. Although the majority of these compounds may not cause direct interference at the ion masses monitored for the PCDD/PCDF, they can overload the capillary GC column or cause suppression of the ionization current in the mass spectrometer source. Column overloading often causes poor chromatographic peak shape which lowers the effective chromatographic resolution. Ion current suppression causes a momentary decrease in the mass spectrometer sensitivity. This can be most easily observed by monitoring an ion mass that is produced from a compound that is continously introduced into the ion source at a constant level. A decrease in intensity of this compound will indicate ion supression. Our procedure for monitoring ion current suppression is discussed in the Analysis Section (page E-7).

TABLE 1. EXTRACTION METHODS AND SOLVENTS

Matrix	Extraction Method	Extraction Solvent
Fly Ash	Soxhlet	Benzene
XAD-2 Resin	Soxhlet	Dichloromethane
Silica Gel	Soxhlet	Dichloromethane
Soil	Soxhlet	Benzene
	Mechanical Mixing	Hexane/methanol
Fish Tissue	Alcoholic KOH Digestion[a]	Hexane
Adipose Tissue	Alcoholic KOH Digestion[a]	Hexane
Water	Liquid-Liquid	Dichloromethane
Oils	Alumina Column	Hexane

a Room temperature if Cl_5-Cl_8 PCDD/PCDF isomers are included. Reflux (80 C) if only TCDD isomers are included.

Liquid chromatography is usually employed to remove coextracted interferences from the extract. The process consists of eluting the extract through two adsorption columns. The first column illustrated in Figure 1 contains alternate layers of activated silica gel, 44% concentrated sulfuric acid on silica gel, and 33% 1 M sodium hydroxide on silica gel. Typically this column is eluted with hexane, however, we have modified the elution and use 15 ml of hexane followed by 10 ml 1:1 (v/v) mixture of hexane and benzene. The use of an aromatic solvent provides PCDD/PCDF recoveries near 100% and decreases the volume of elution solvent to approximately 25 ml.

The eluate from the multilayered silica column is collected, concentrated, and solvent exchanged into 1 ml of hexane. The hexane solution is then added to the top of a column containing 18 grams of basic alumina activated at 300 C for 90 minutes (Figure 1). This column is eluted with 25 ml of hexane, 20 ml of hexane/carbon tetrachloride (1:1, v/v), and 20 ml of hexane/dichloromethane (1:1, v/v) in sequence.

The hexane/dichloromethane eluate contains the halogenated aromatics including all the PCDD and PCDF isomers. It is collected in a silanized 18 ml concentrator tube, and concentrated to near dryness at 30 C using a gentle stream of ultrapure nitrogen. The sides of the tube are rinsed with 1 ml of dichloromethane and concentrated to 50 µl. This rinsing process is conducted three times. The final 50 µl volume of the concentrator tube is allowed to evaporate to dryness on standing without the use of the nitrogen stream. The residue is dissolved in 20 µl of decane and mixed by vortex. The decane solution is stored at 0 C and protected from light until it is analyzed. It is essential to conduct the concentration by this procedure, especially using silanized glassware, rinsing, and final evaporation without a nitrogen stream, to minimize the loss of the picogram quantities of dioxins and furans present during their analysis at the parts-per-trillion level.

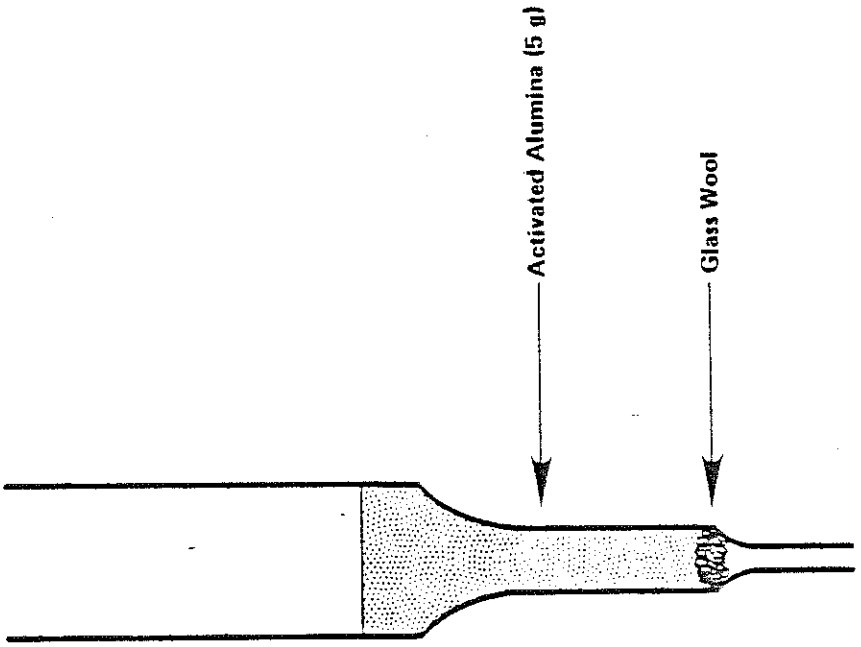

FIGURE 1. ACTIVATED ALUMINA COLUMN

If necessary, a third column can be used to remove specific interferences such as PCBs from tetrachlorinated dioxin isomers. This additional column consists of 5 grams of florisil activated at 165 C for 24 hours. The column is eluted with 25 ml of hexane, 25 ml of 6 percent dietylether in hexane, 20 ml of 30 percent dichloromethane in hexane. The last eluate contains the tetrachlorinated dioxin isomers and is collected, concentrated and stored using the same procedure described above. This procedure has been optimized for the isolation of tetrachlorinated dioxin isomers, particularly 2,3,7,8-TCDD. Further refinement to the method is necessary to isolate the higher chlorinated species.

Analysis of PCDD/PCDF by Gas Chromatography/ High Resolution Mass Spectrometry

To achieve the ultimate detection limit and maximize chromatographic resolution it is important to interface the capillary column directly into the ion source of the mass spectrometer. Although zero dead volume couplers and efficient transfer lines are available, they still degrade chromatographic resolution because of adsorption. This degradation cannot be tolerated if isomer specific analyses are required. An example of the chromatographic resolution obtained by direct interface of the capillary column to the mass spectrometer is shown in Figure 3. Note the uniform symmetry of the GC peaks and the complete resolution of 2,3,7,8-TCDD from 1,4,7,8-TCDD and 1,2,3,4,-TCDD. Typically, the chromatographic peak widths at half height are less than 5 seconds. This resolution is required to eliminate the detection of false positives because of chromatographic coelution of other TCDD isomers.

The mass spectrometer is operated in the electron impact ionization mode at a mass resolution of 10,000-12,000 (M/ΔM, 10% valley definition). This mass resolution is sufficient to resolve the PCDD/PCDF isomers from most of the interferences. A minimum of two ion masses are monitored by multiple ion detection for each of the PCDD/PCDF

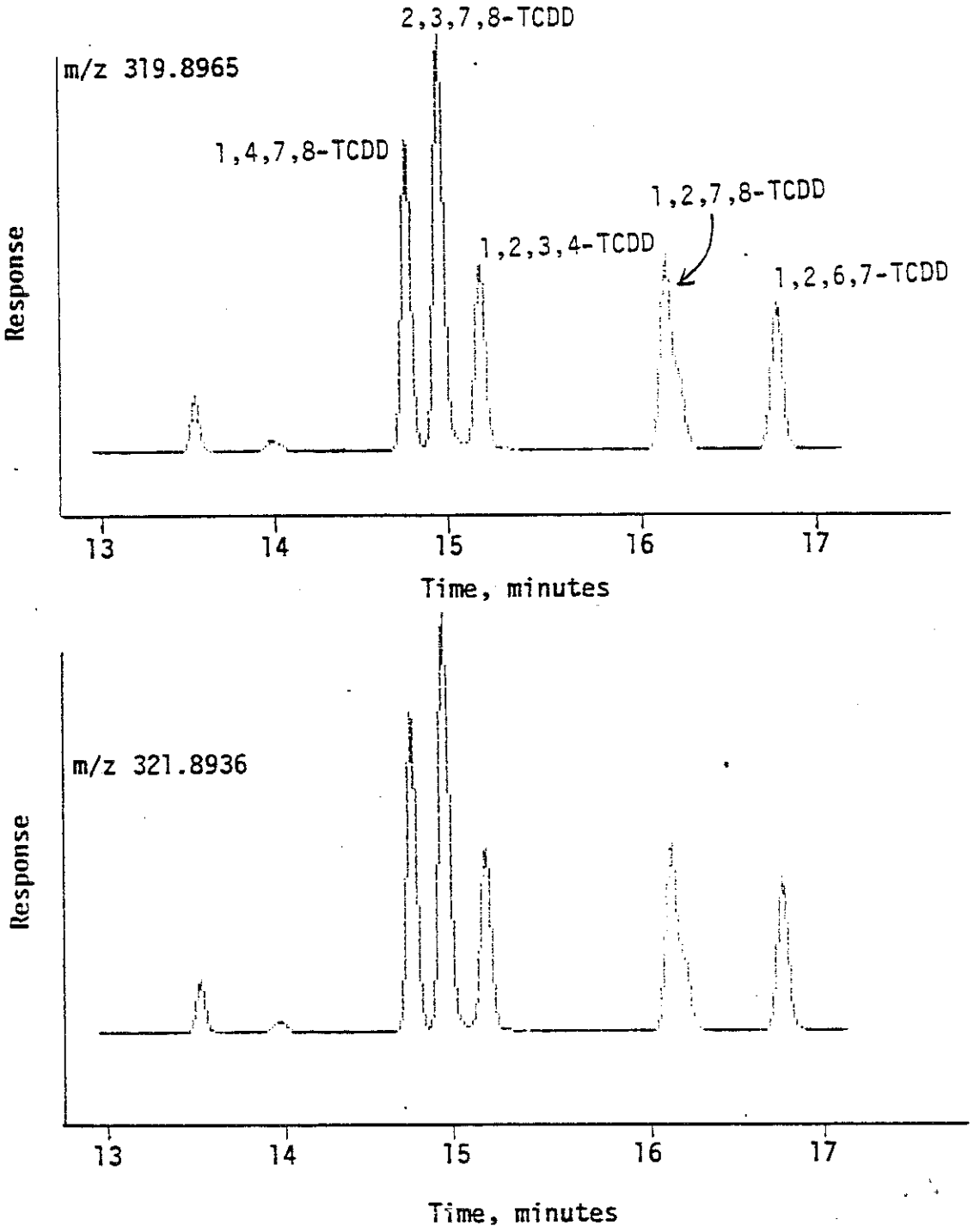

FIGURE 2. SELECTED ION CURRENT TRACES ILLUSTRATING CHROMATOGRAPHIC RESOLUTION

standard. Isotope ratios can thus be calculated and compared with their theoretical values to confirm their identify.

Monitoring a reference lock mass is used in the analysis procedure and provides two advantages. First, it corrects for any mass drift that may occur due to temperature or electrical variations. The data system calculates the centroid of the reference lock mass and applies corrections due to drift to the analyte masses which are being monitored. Most modern mass spectrometers are stable on a short term basis (1-10 minutes), but can drift off the center of the mass peak during the course of a 30-60 minute analysis. This drift will reduce the apparent sensitivity of the mass spectrometer and also allow compounds to interfere with the analysis. The second advantage is that with a lock mass it is possible to detect ion current suppression caused by the elution of high level interferences at ion masses that are different from the PCDD/PCDF. By monitoring the lock mass intensity, which should remain constant, it is easy to observe ion supprerssion due to the complexity of the matrix. If severe ion suppression is observed, it is necessary to reprocess the extract to remove the interfering material.

A positive response for a PCDD/PCDF requires that the following criteria be satisfied:

- Simultaneous response at both analyte masses monitored
- Signal to noise ratio greater than 2.5:1.0 for both ions
- Correct chlorine isotopic ratio ($\pm$ 10%)
- Retention time within $\pm$ 1 second of an authentic reference standard (if available)
- Retention time within elution window determined by analyses of standards.

Ideally, each of the 210 PCDD/PCDF isomers should be quantified against the instrument response of their corresponding stable isotope internal standard as a reference, By this method the errors due to extraction efficiencies and clean up losses would be corrected for

each isomer. In addition, the relative response factors would be essentially 1.00. Due to the limited number of isotopically labelled standards, this is not possible. Two standards, 2,3,7,8-tetrachlorodibenzo-p-dioxin-$^{13}C_{12}$ (2,3,7,8-TCDD-$^{13}C_{12}$) and octachlorodibenzo-p-dioxin-$^{13}C_{12}$ (OCDD-$^{13}C_{12}$) must be used for quantifications of all 210 isomers. Thus it is necessary to choose the internal standard that most closely approximates the extraction of the PCDD/PCDF isomers being quantified and to apply a correction for the relative response factor. The relative response factors are determined from analyses of standard solutions containing the internal standards and representative isomers of each chlorination class. The tetrachloro-through pentachloro-PCDD/PCDF isomers are quantified using 2,3,7,8-TCDD-$^{13}C_{12}$ while the hexachloro- through octachloro- PCDD/PCDF are quantified using OCDD-$^{13}C_{12}$. The equation used for quantification is:

$$\text{Concentration, ppt} = \frac{\text{Area of the PCDD/PCDF} \times \text{Quantity of Internal Standard}}{\text{Area of the Internal Standard} \times \text{Weight of Sample(g)} \times \text{Reponse Factor.}}$$

The area of the PCDD/PCDF isomer is the sum of areas of the two ion masses being monitored for the particular PCDD/PCDF class. The area of the internal standard is the sum of the two corresponding ion masses of the standard.

Reporting

The report format is usually designed to meet the requirements of the specific program. It is important however, that as a minimum, all reports contain the following information:

(1) Mass resolution of the mass spectrometer including a definition of resolution (e.g., M/ΔM, 10% valley),

(2) Gas chromatographic column employed for isomer

(3) Criteria used to identify the PCDD/PCDF isomers,

(4) Method used to quantify the PCDD/PCDF isomers,

(5) Description of standards used and the values of relative response factors,

(6) Limit of detection for PCDD/PCDF isomers which were not detected, including method of calculation, and

(7) Reconstructed ion chromatograms for each of the monitored ion masses of the analysis.

QUALITY CONTROL PROGRAM

Typical QC requirements include one method blank, one duplication, one native spike, and one reanalysis per group of ten samples. Additional QC includes the analyses of PCDD/PCDF isomer mixtures to verify chromatographic separation efficiency, analysis of standards to verify the absolute sensitivity of the HRGC/HRMS, and checks of the mass resolution using perfluorokerosene. Corrective action is taken if any of the QC parameters fall outside of the requirements of the specific program. QC criteria for a program to determine 2,3,7,8-TCDD at the lowest possible detection limits (1-10 ppt) are as follows:

- All method blanks below the Detection Limit,
- Mass resolution between 10,000-12,000 (M/ΔM, 10% valley),
- Complete chromatographic resolution of a standard TCDD isomer mixture (e.g. 1,2,3,4,-TCDD, 1,4,7,8-TCDD, and 2,3,7,8-TCDD),
- Duplicate analyses within 50% relative difference, and
- Native spiked analysis within 50% of correct value.

All criteria must be satisfied for the results of the analyses to be in control.

APPENDIX F

SAMPLE PREPARATION FOR METALS ANALYSIS

APPENDIX F

SAMPLE PREPARATION FOR METALS ANALYSIS*

For the determination of total metals the sample is acidified with 1:1 redistilled HNO_3 to a pH of less than 2 at the time of collection. The sample is not filtered before processing. Choose a volume of sample appropriate for the expected level of metals. If much suspended material is present, as little as 50-100 ml of well mixed sample will most probably be sufficient. (The sample volume required may also vary proportionally with the number of metals to be determined.)

Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 ml of conc. redistilled HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3 ml portion of conc. redistilled HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of redistilled 1:1 HCl (5 ml/100 ml of final solution) and warm the beaker to dissolve any precipitate or residue resulting from evaporation. (If the sample is to be analyzed by the furnance procedure, substitute distilled HNO_3 for 1:1 HCl so that the final dilution contains 0.5% (v/v) HNO_3.) Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis. Concentrations so determined shall be reported as "total".

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* United States Environmental Protection Agency, 1983, Methods for Chemical Analysis of Water and Wastes. Method 200.7 U. S. Environmental Protection Agency, Cincinnati, EPA-600/4-79-020, Revised 1983.

APPENDIX G

INDUCTIVELY COUPLED PLASMA - OPTICAL EMISSION SPECTROMETRY (ICAP)

APPENDIX G

INDUCTIVELY COUPLED PLASMA - OPTICAL EMISSION SPECTROMETRY (ICAP)*

The Jarrell-Ash Model 975 Plasma AtomComp Spectrometer in operation at Battelle is a direct reading system using a DEC PDP-8A control processing unit. The J-A Plasma Analytical Language PAL-2 software system provides the required operating functions and computations in the units of interest; the dual DEC floppy disks provide 128 kilobytes of disk storage capacity with 483 ms average access time. Background correction of individual spectral lines is automatically performed by the two-point Spectrum Shifter operated under computer control. Interelement correction factors have been determined for each channel and are automatically effected.

The Model 975 ICAP may be equipped with up to 48 individual channels. The selection of the 30 specific channels for the unit in operation in Battelle's laboratories was based on the frequency of projected needs for each metal. The 30-channel assembly with selected photomultipliers installed in the 975 Plasma AtomComp Spectrometer includes: aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, nanganese, mercury, molybdenum, nickel, phosphorous, selenium, silver, sodium, strontium, thallium, tin, titanium, vanadium, yttrium, and zinc. Thirteen of these 30 channels provide for the simultaneous analysis of all inorganic constituents currently on EPA's priority pollutant list. An additional element of choice may be selected by using the Mark V, N+1 channel option. The N+1 channel may also be used to present data as a continuous signal to an external recording device. A peristaltic pump is used for sample uptake to minimize the effects of changing viscosity and high salt content. The selectivity and sensitivity of the ICAP coupled with the ability to perform simultaneous analyses make this tool requisite for state-of-the-art trace metal work. The ICAP is used by Battelle scientists as a research tool for determinations of trace metals in water, sediment, aqueous and solid industrial wastes, hazardous wastes, and biological materials.

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* United States Environmental Protection Agency, 1983, Methods for Chemical Analysis of Water and Wastes-Method 200.7, U.S. Environmental Protection Agency, Cincinnati, EPA-600/4-79-020, Revised 1983.

APPENDIX H

PCB ANALYSIS BY GC/ECD

APPENDIX H

PCB Analysis by GC/ECD*

Extracts of leachates and sludge in hexane were analyxed by gas chromatography with electron capture detection (GC/ECD) for the presence of PCB's. The sample extracts were compared withknown Arochlor PCB standards. The gas chromatographic conditions used for the analyses were as follows:

Column: 6' x 2 mm glass; 1.95% OV-17, 1.50% QF-1
on 100/120 mesh Chromasorb W
Column Temperatures: 165° and 210°C
Injector Temperature: 225°C
Carrier Gas: 90/10 An/Methane @ 25 cc/min
Detector: Ni^{63} @ 300°C
Injection Volume: 2 µL.

Samples were run at both 165° and 210°C to analyze for both the low and high boiling range of Arochlors. No PCBs (as Arochlors) were detected in the leachate extracts at levels greater than 10 ppb. The sludge extracts were very complex and positive confirmation for the presence of PCBs could not be made using GC/ECD. The analysis showed the possible presence of from between 50 to 350 ppm of PCBs but numerous interfering components made positive identification impossible. Sample cleanup using Florisil column chromatography did not remove the interferences.

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* United States Environmental Protection Agency, 1982, Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, Second Ed. Method 8080. U.S. Environmental Protection Agency Office of Solid Waste, Washington, D.C. SW-846.

APPENDIX I

Pesticide Analysis by GC/ECD

APPENDIX I

Pesticide Analysis by GC/ECD*

Extracts of leachates and sludge in hexane were analyzed by gas chromatography with electron capture detection (GC/ECD) for the presence of lindane, endrin, methoxychlor, and toxaphene. The gas chromatographic conditions used for the analyses were as follows:

Column: 6' x 2 mm glass; 1.95%)V-17, 1.50% QF-1
on 100/120 mesh Chromasorb W.
Column Temperature: 200°C
Injector Temperature: 225°C
Carrier Gas: 90/10 Argon/Methane @ 25 cc/min
Detector: Ni^{63} @ 300°C
Injection Volume: 2 µL.

* United States Environmental Protection Agency, 1982, Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, Second Ed. Method 8080. U.S. Environmental Protection Agency Office of Solid Waste, Washington, D.C. SW-846.

APPENDIX J

BENZIDINE ANALYSIS

BENZIDINE ANALYSIS

Fifty microliter aliqouts of the aqueous leachate of sludge extract were analyzed using the following HPLC conditions:

Column:	Lichrosorb RP-2, 5 micron, 250 x 4.6 mm
Solvent:	50% acetonitrile, 50% 0.1 M sodium acetate
Flow:	1 ml/min
Detector:	Electrochemical detector with glassy carbon electrode @ 0.8 volts.
Reference:	EPA Method 605 -Benzidines

$1.4

Chemical Waste Management, Inc.
3003 Butterfield Road
Oak Brook, Illinois 60521
312/654-8600

May 2, 1984

Dr. Richard Shank
OHIO ENVIRONMENTAL PROTECTION AGENCY
361 East Broad Street
Columbus, Ohio 43210

Dear Rick:

Attached is a copy of an interim status report which was provided by Battelle Columbus Laboratories detailing the initial results. The report is preliminary in nature; however, it does contain the data for the chemical analysis on the sludge materials in the surface impoundments. I have excluded the financial information and the detailed methods.

Battelle's schedule was to perform the EP extracts of the samples on April 26 and to begin the analysis. Our understanding is that Battelle will have no delays in analytical work because the scheduled time has been reserved in the analytical laboratories. Bruce Vigon has told us to expect the report to be completed on or around May 15. We will be providing you with a copy of the report as soon as it is available.

Very truly yours,

George Vander Velde

GV/kg

cc K. Cherry
G. Simmons
J. Miller
J. Homsy
L. Tickamin
K. Trent
L. Tinnin
M. Walker

— Bremer/Young
— Banaszek/Brossman
— Muno/Karl
— McPhee
— Willey (DOJ)
—

INTERIM REPORT
(Phase I/Phase II)

on

WASTE POND SLUDGE STABILIZATION ALTERNATIVES ASSESSMENT

to

CHEMICAL WASTE MANAGEMENT, INC.
OAK BROOK, ILLINOIS

April 19, 1984

INTERIM REPORT
(PHASE I/PHASE II)

on

WASTE POND SLUDGE STABILIZATION
ALTERNATIVES ASSESSMENT

to

CHEMICAL WASTE MANAGEMENT, INC.
Oak Brook, Illinois

April 19, 1984

from

BATTELLE
Columbus Laboratories

OBJECTIVES

The hazardous waste facility at Vickery, Ohio, owned by Chemical Waste Management, Inc., contains several large lagoons that have been used for the temporary storage of waste oil and other materials. These materials range from liquids to semi-solids and have, over the years, caused a layer of contaminated sludge to build up on the pond bottom.

Chemical Waste Management, Inc., plans to close one of these ponds permanently and is being required to demonstrate the effectiveness of the pond closure program in attenuating these contaminants to levels below regulatory concern. As a part of the engineering program, Chemical Waste Management, Inc., has developed recipes for four alternative sludge stabilizations which may prove effective in controlling leachate production and quality.

The objectives of this research are threefold:

(1) Characterize the unstabilized sludge and raw solidification matrix materials by state-of-the-art chemical analytic techniques to establish reference baseline conditions for subsequent stabilization methodology evaluations,

(2) Prepare test specimens for leaching experiments that will be consistent with current EP toxicity methodology as described in the Federal Register, May 19, 1980, and amplified by EPA

Publication SW-846 "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" (1982), and

(3) Analyze the effectiveness of the four stabilization alternatives in two ways. First, compare the relative attenuation of each alternative to each other and to the unfixed reference baseline. Second, where reasonable contaminant specific water quality concentrations can be established by their EP toxic levels or a 30X multiplier of the ambient water quality criteria, compare the leachate concentrations to these target values.

This report constitutes an interim summary of work accomplished from contract initiation through the completion of Phase II work.

Phase I - Unfixed Sludge and Raw Materials Characterization

Samples of waste pond sludge and five fixation system components--kiln dust, beet tailings, fly ash, virgin clay and sulfate sludge--were subjected to extraction and analysis. Two samples of sludge and the raw fixation materials were processed through the EP leaching procedure as shown in Figure 1. Details of the protocol are described in Appendix A. A third sludge sample was analyzed by exhaustive extraction to determine the total contaminant content. In this way an estimate could be made of the availability of a contaminant.

Leachate or extract was analyzed for the following classes of contaminants using approved EPA protocols as indicated:

- Volatile organic priority pollutants (Method 624 Purge and Trap followed by GC/MS)
- 2,3,7,8 TCDD (GC/MS)
- Pesticides (Method 608 GC-ECD)
- Polychlorinated biphenyls (Method 608 GC)
- EP Toxicity Metals (Method 8.8.3-ICAP/AA).

Detailed descriptions of the sample preparation and analysis protocols are contained in the appendices.

Phase I Results

Analysis results for the raw materials were examined for two purposes. First, high levels of contaminants in the raw materials would be undesirable. Contributions of contamination from the fixation materials would place additional demands on the stabilization process. Second, if contaminants are not removed from either the fixative agents or the sludge, then Phase III analysis will not need to incorporate these parameters.

Volatile Organic Priority Pollutants. The Method 624 results from the analysis of the eight samples and three method blanks are shown in Table 1. The EP leachate analysis for the two sludge samples indicates the presence of detectable concentrations for several chlorinated aliphatic hydrocarbons. In this class of compounds the concentrations of 1,2 dichloroethane and chloroform were significantly higher than the other analytes and may be good indicators of attenuation performance.

Four aromatics were also detected, with toluene and chlorobenzene present in concentrations above one mg/l. Stabilization performance for those recipes containing clay or other siliceous material will be closely watched because of reported shrinkage problems and poor material compatibility.

Several organic species were detected in the EP extract that were not found in the methanol extract. In view of the much higher method detection limit (MDL) for the methanol extract (50 µg/g versus 5-10 µg/l in the EP extract), these findings should not be construed as a lack of accuracy.

Partition coefficients and extraction efficiencies were computed for the eight compounds where solid phase concentrations were detectable. Partition coefficients (concentration in solid phase divided by concentration in liquid (EP extract) phase) and extraction percentages confirmed that aqueous acid is not a severe leaching agent for hydrophobic matrices and contaminants such as those examined in this study. Extraction efficiencies averaged 1.2 percent and did not exceed 4.7 percent (chloroform).

With the exception of methylene chloride (suspected to be due to laboratory atmosphere contamination), only trace concentrations of VOCs were present in the raw materials. These ingredients to the overall recipes should

ANALYTE	RAW SAWDUST (a)	RAW SAWDUST (a)	RAW SAWDUST (b)	FAST SLUDGE	KIDNEY LSNT	VOLCANIC RAGYIN	SSULUDGE FDAGTE	BTEA EIL NG S	MB EL TA HN OK D1	MB EL TA HN OK D2	MB EL TA HN OK D3
	CONCENTRATION, ppb (except as noted)										
CHLOROMETHANE	ND	ND	ND (c)	ND	ND	ND	ND	ND	ND	ND	ND
BROMOMETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
VINYL CHLORIDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CHLOROETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
METHYLENE CHLORIDE	340	150	ND	>220	>170	>100	4.2	>150	0.3	0.4	0.3
ACETONE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
ACROLEIN	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TRICHLOROFLUOROMETHANE	ND	ND	ND	0.3	0.5	ND	0.2	ND	ND	ND	ND
ACRYLONITRILE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-DICHLOROETHYLENE	27	37	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-DICHLOROETHANE	35	36	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-DICHLOROETHYLENE	ND	ND	ND	ND	ND	0.4	ND	ND	ND	ND	ND
CHLOROFORM	540	610	61	0.7	0.7	0.3	1.0	3.0	0.2	0.2	0.1
1,2-DICHLOROETHANE	850	930	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-TRICHLOROETHANE	260	320	258	2.6	3.0	2.0	3.9	1.5	1.2	ND	ND
CARBON TETRACHLORIDE	20	23	ND	ND	ND	ND	ND	ND	ND	ND	ND
BROMODICHLOROMETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-DICHLOROPROPANE	ND	9.3	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-DICHLORO-1-PROPENE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TRICHLOROETHYLENE	78	97	86	ND	0.8	ND	0.2	0.3	ND	ND	ND
BENZENE	200	230	56	ND	0.7	0.8	ND	ND	ND	ND	ND
DIBROMOCHLOROMETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2-TRICHLOROETHANE	7.0	7.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-CHLOROETHYL VINYL ETHER	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BROMOFORM	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-TETRACHLOROETHANE	12	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TETRACHLOROETHYLENE	57	72	188	ND	0.5	ND	ND	ND	ND	ND	ND
TOLUENE	1400	1700	1180	0.7	1.2	0.4	0.7	0.5	0.7	0.2	0.6
CHLOROBENZENE	1200	1500	1040	ND	ND	0.1	0.3	ND	ND	ND	0.2
ETHYLBENZENE	57	68	124	ND	ND	ND	ND	ND	ND	ND	ND

(a) EP Extract (100 gram sample)
(b) Methanol Extract
(c) Concentrations in this column are in mg/kg (ppm)

TABLE 1. ANALYSIS OF RAW MATERIALS AND SLUDGE VOLATILE PRIORITY POLLUTANTS-METHOD 624 SAMPLE

prove acceptable from the standpoint of not creating stabilization matrix problems.

Dioxin, Benzidines, Pesticides and PCBs. This category of contaminants was even less efficiently extracted than the Method 624 organics (Table 2). Dioxin was present at less than 3 ng/l and PCBs were less than 10 µg/l in the EP leachate. None of the pesticides were present and the analyses for benzidines has been deferred until Phase III.

The exhaustive analysis (using high resolution mass spectrometry) of 2,3,7,8-TCDD indicated the presence of this isomer at 87 ng/g. Therefore, relative attenuation of TCDD by each of the four methods cannot be established with the EP protocol. Although the interferences present additional confirmational problems for the PCBs, a similar negative comment applies to their use as an indicator of fixation potential.

Metals. Four of the eight EP toxicity metals were detected in the EP leachate from the raw sludge (Table 3). However, only lead was present in moderately elevated concentrations. As was observed for the Method 624 extraction efficiencies, most of the considerable metal content (especially chromium and lead) was unavailable given the leaching conditions of the experiment.

Of the raw materials, the fly ash exhibited very high leachate concentrations of lead and moderately high concentrations of barium, chromium, and mercury. The remaining raw materials had detectable barium concentrations but EP toxicity concentrations are well above the observed levels. The clay also leached (barely) detectable amounts of lead and a trace of mercury was found in the beet tailings.

Phase II

Samples of each of the four recipes were made up on April 12 according to the procedure provided by Chemical Waste Management, Inc. Approximately one kilogram of each was prepared by mixing the ingredients with a Teflon-coated spatula for 15 minutes. The mixture was allowed to set for several hours and then packed into Teflon tubes for airing. A small amount of

TABLE 2. ANALYSIS OF RAW MATERIALS AND SLUDGE 2,3,7,8-DIOXIN, BENZIDINES, PESTICIDES AND PCBs

ANALYTE	SAMPLE: RAW WUDGE	RAW WUDGE	RAW WUDGE	FLY ASH	KILN DUST	VIRGIN CLAY	SLUDGE AGITEE	BEETLING
	CONCENTRATION, ppb (except as noted)							
2,3,7,8 TETRACHLORODIBENZO-DIOXIN	<0.003	<0.002	87	—	—	—	—	—
BENZIDINE	——— TO BE COMPLETED DURING PHASE III ———							
3,3'DICHLOROBENZIDINE	——— TO BE COMPLETED DURING PHASE III ———							
ENDRIN	<2	<2	<10 (c)	<0.02	<0.02	<0.02	<0.02	<0.02
LINDANE	<2	<2	<10 (c)	<0.02	<0.02	<0.02	<0.02	<0.02
METHOXYCHLOR	<10	<10	<50 (c)	<0.10	<0.10	<0.10	<0.10	<0.10
TOXAPHENE	<20	<20	<100 (c)	<0.20	<0.20	<0.20	<0.20	<0.20
2,4-D								
2,4,5-TP (SILVEX)								
PCBs(as Arochlor mixture)	<10	<10	<500 (c)	<0.10	<0.10	<0.10	<0.10	<0.10

(a) EP Extract (100 gram sample)
(b) Solvent Extract
(c) Concentration in mg/kg (ppm)

ANALYTE	SAMPLE								
	RAW SLUDGE	RAW SLUDGE	RAW SLUDGE	FLY ASH	KODIAK SLAG	VICINITY SOIL	SSULFUR	BITEAL INGS	MBELTAHNOKD
	CONCENTRATION, ppb (except as noted)								
ARSENIC	<100	<100	41 (c),(d)	<100	<100	<100	<100	<100	<100
BARIUM	76	64	63 (c)	630	390	460	110	140	12
CADMIUM	12	9	9.1 (c)	<5	<5	<5	<5	<5	<5
CHROMIUM	58	48	330 (c)	580	<10	<10	21	<10	<10
LEAD	550	560	380 (c)	73300	<50	57	<50	<50	<50
MERCURY	<0.3	<0.3	5.6 (c)	6.80	<0.3	<0.3	<0.3	4.52	<0.3
SELENIUM	<100	<100	9.3 (c)	<100	<100	<100	<100	<100	<100
SILVER	<10	<10	0.9 (c)	<10	<10	<10	<10	<10	<10

(a) EP Extract (100 gram sample)
(b) Acid Digestion Extract
(c) Concentrations in mg/kg (ppm); value is mean of duplicate analyses
(d) May be biased high due to aluminum interference

TABLE 3. ANALYSIS OF RAW MATERIALS AND SLUDGE
METALS

additional material was placed in a beaker for observation during the two-week curing period.

Samples will be ready for grinding, sieving, and extraction on April 25.

Costs

Program costs to date are shown in Figure 2. Phased costs have been revised to reflect altered project milestone schedules. Even so, expenditures have been slightly lower than anticipated.

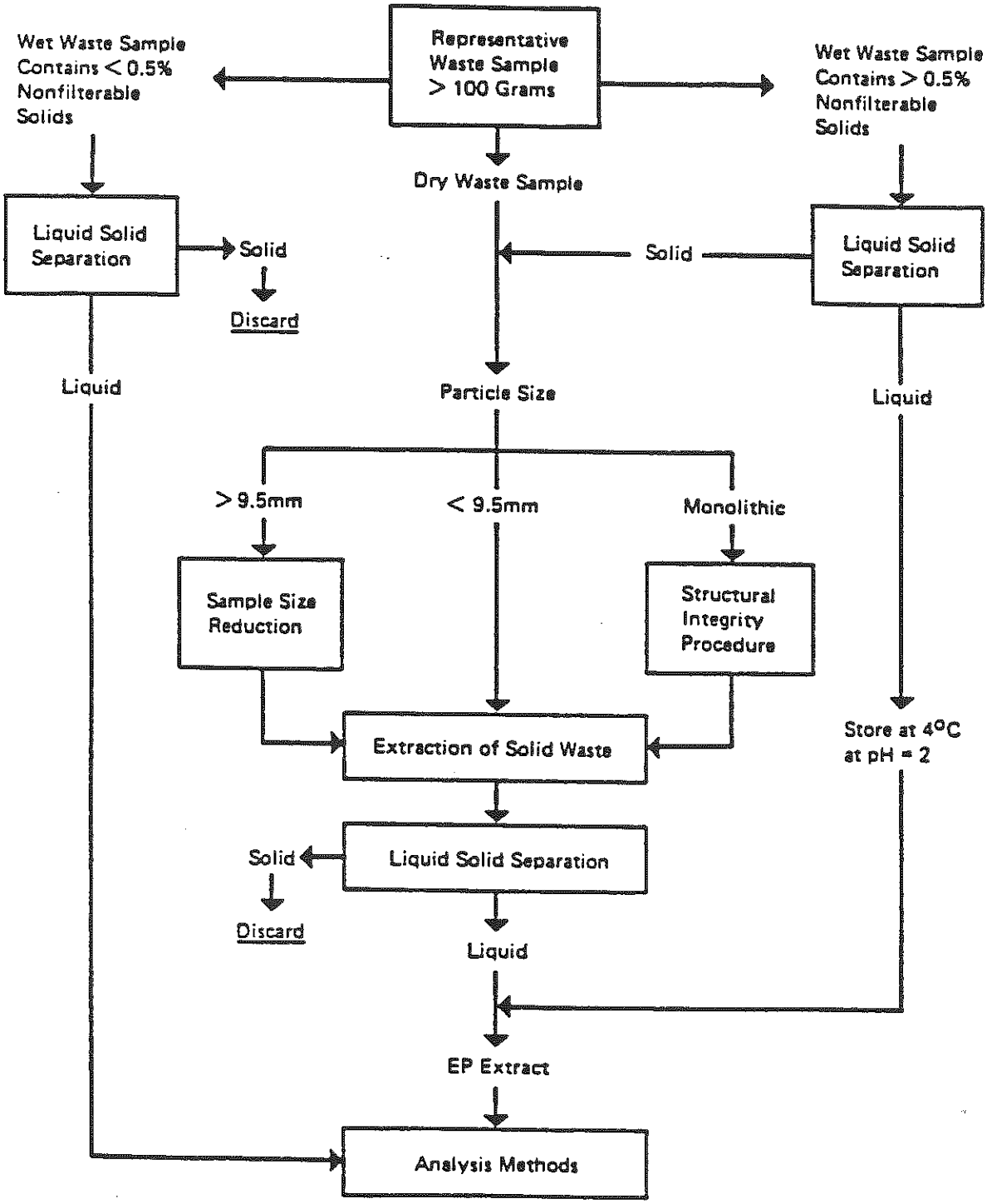

Figure 1. Extraction Procedure Flowchart.